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DYNAMIC HYPERFILTRATION MEMBRANES

FOR

HIGH-TEMPERATURE SPACECRAFT WASH WATER RECYCLE

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February, 1978

FINAL REPORT



Prepared for:

Johnson Space Center
Houston, TX 77058

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1.0 SUMMARY

Hyperfiltration is a technology considered for separation of solutes leading to the recycle of spacecraft wash water. The dynamic membrane has been considered a candidate because of its high temperature capability, its tubular (low plugging) configuration, and its adaptability to the low flow situations demanded by power-limited processing of small batches.

The effort reported herein follows a study of the effect of processing parameters on the separation efficiencies. The earlier study revealed reasonably high separation of inorganics and a high separation of organics except for urea. Also parametric data for the effect of pressure, temperature, velocity, and concentration were measured, allowing design calculations to be initiated.

The search for a tube having excellent mechanical strength was conducted leading to membrane formation on a porous stainless steel tube. The formation procedure was modified to accommodate the steel tube corrosion susceptibility and the membranes on stainless steel tubes were found to be essentially equivalent to those of past experience.

One stainless steel tube and three ceramic tubes were selected for a ninety-day test program. The membranes were operated daily for about a 50% duty cycle and were subjected to an amount of new wash water per unit area as is expected in full-scale operation. The membranes were operated with a number of velocity conditions; at low and high concentration; and with variations in operating temperature. Parametric data were taken at the end of testing to compare with results prior to long-term operation.

All four tubes successfully completed the test program. The solute rejection of two tubes decreased by an amount not considered serious, while the other two remained essentially unchanged. All membranes became more sensitive to concentration, and the production rate declined generally with occasional remissions. The flux decline after 300 hours of operation was slight enough that it is considered possible to design a control system to operate within the subsequent variation.

The permeate water produced was averaged mathematically for various solute concentrations. Inorganics were rejected satisfactorily as were organics generally. Some violation of zero foaming in 15 seconds was predictable and the ammonia level was exceeded. Although the urea may or may not be controlled to its 50 mg/l limit, the presence of any substantial fraction of the limit in the hot permeate water is estimated to result in an ammonia control problem.

Means for control of urea/ammonia were evaluated. Xanthidrol, iodine, and hypochlorite were bench tested while nitrites and perchlorates were screened from consideration. Xanthidrol was found effective at pH below about 4 but not effective at ordinary pH. Iodine was only 25% effective, but sodium hypochlorite was highly effective. Decomposition of residual hypochlorite by cobaltous hydroxide and powdered cobalt were found effective.

A computer program was constructed to evaluate the weight penalty effect of system design considerations. The program predicted minimum penalty in a non-recirculating, low terminal velocity configuration. The optimum temperature was predicted to be 75°C, and the best membrane flux was about 1.0×10^{-5} m/sec, which is about the level observed at the end of ninety-day testing.

A module was designed and constructed having 196 tubes, 2 mm diameter and 30 cm long. Membranes were formed on the module which had an overall target value performance level at least twice. Due to structural/mechanical design difficulties, a number of fractures of one of the members occurred, resulting finally in a deformed header which was incapable of maintaining a seal required for operation. No useful wash water testing was therefore performed. However it was observed that the membranes were successfully formed in the very high l/d configuration. The failure of the module was a structural design problem which is unrelated to any membrane problem.

Finally six tubes of a possibly improved configuration were evaluated and found to be not superior to the original tubes. The manufacturer's tube with a 0.5 micron pore rating are still considered as good as we can specify.

2.0 INTRODUCTION

Extended manned missions in space produce substantial requirements for water. These requirements are prohibitive without recycle capability. In 1970 tests were conducted [1]^a to evaluate the various components of a proposed life support system, including water management. It has been recognized that wash water is easier to treat than is urine and designs have centered on a system to recycle wash water and another system to recycle both urine and any blowdown from the wash water system. This latter is a relatively small flow system, a leading approach being a vapor compression/distillation (VCD) process. In Reference 1, the wash water recycle utilized filtration, ion exchange, and carbon adsorption. During this test problems were encountered with control of organics which built up to levels beyond allowable values.

Further development efforts have emphasized membrane separation for improved performance in recycling wash water. Several contracts through OSW and NASA sought to evaluate commercial membrane units, e.g., see References 2 and 3. Also a feasibility test [4] of a high-temperature membrane developed by the Oak Ridge National Laboratory (ORNL) [5] showed promise for the application. The primary benefits of the dynamic membrane were: (1) high-temperature capability, (2) tubular configuration, (3) adaptability to small scale, and (4) high flux.

Based on the preliminary results a program was initiated to design a test unit to satisfy the requirements for the application. An early segment of the work involved parametric testing. The data are included herein as Appendix A for convenience. The body of the report discusses the development of a mechanically suitable tube for membrane formation, a ninety-day test, an optimization analysis, methods for urea/ammonia control, and module breadboard design and testing.

^a Numbers in brackets denote references shown in Section 5.0.

3.1 STAINLESS STEEL FOR MEMBRANE SUPPORTS

The original objective of this project was to investigate the properties of the zirconium oxide polyacrylic acid membrane (hereafter, the dynamic membrane) as applied to spacecraft wash water. No attempt was anticipated to investigate new support materials since previous investigators had spent considerable effort in determining the best obtainable. Although membrane suitability based on the parametric testing appeared positive (Appendix A and Reference 6), some concern was expressed over the applicability of the ceramic tube in the mechanical environment of flight. A sample of a sintered steel tube was obtained and attempts were made to form a membrane on it. The results were not outstanding (65% rejection) but offered encouragement. Previous formation efforts on similar tubes had been unsuccessful [7] for various reasons. The accepted opinion at that time was that the pore sizes of the metal tube were much larger than those of the ceramic tube or of the Millipore/Acropore surface.

Pore size is commonly measured by actual diameter or by particle size retention. It is generally accepted that particles an order of magnitude smaller than the actual pore size may be retained by a filter. The Oak Ridge Laboratory personnel normally use the pore size as the pertinent feature. The metal tubes were rated by particle retention and scaled to small-pore observations using a bubble point correlation. A tube's bubble point is that pressure which causes bubbles to appear at the tube's surface when submerged. The bubble point pressure for tubes is expected to vary inversely with the pore radius if the bubble radius and pore radius maintain an equal ratio, i.e., the pores are geometrically similar. Using the bubble point variation and a single correlation of a bubble point with a particle retention observation, the pore size may be determined. Oak Ridge personnel knew that the 0.5 micron metal tubes really had pores about 5 microns which were much larger than the 0.2 to 1.0 micron size range deemed necessary for membrane formation. They, therefore, were not surprised to be unsuccessful in membrane formation with such tubes.

It became clear that during formation on stainless tubes iron was being removed from the tube and system. A quick estimate of the metal surface area in the tube showed it to be much larger than the other fluid-wet portions of tubing, etc. Therefore, the iron removal rate during $\text{pH} \approx 2$ in 0.05 molar chloride solution was indeed much greater than in the same system with the ceramic substrates. To counter this the formation chemicals were changed to include nitrates in place of chlorides (HNO_3 for HCl , $\text{ZrO}(\text{NO}_3)_2$ for $\text{ZrO}(\text{Cl})_2$, and NaNO_3 for NaCl). Formations subsequently were made on both ceramic and stainless steel substrates with state-of-the-art rejections on the ceramic and reasonably good rejections on the steel membranes. In other attempts in our lab and at Oak Ridge it was found that membranes formed using filter aids,

such as powdered carbon (Regal SR-10), had performances equal to those on ceramics.

A list of our formation attempts is provided in Table 1. The table shows effectively an approach to an asymptotic limit of rejection around 85%. The apparent limit to rejection may be a "learning curve" phenomenon or it could be that the electric charge necessary for membrane formation may depend upon the conductivity or other property of the substrate material.

The following postscript explanation is added concerning the decisions to base the design on bare tube membrane formation. Of the membranes formed in the project, tube #3 of Table 1 was deemed the most satisfactory for testing. It was used in the ninety-day test and is designated #34S according to our formation sequence numbering. Tubes #12 and #13 of Table 1 were the only attempts on the NASA-sponsored project using carbon filter aid, and these attempts showed no improvement over the bare tube formations. The results included as tubes #14 - #21 (from another project) culminated in two of three carbon-aided membranes with competitive performance levels. Experience at Clemson, Oak Ridge National Laboratory, and in a followup Lockheed-Abcor project subsequent to the test program and design phase reported herein have indicated with some confidence that the use of carbon filter aid provides a higher performance level. However at the time of decision the data (Table 1) were not so clear.

We had elected to use our best tube for ninety-day testing so the data gathered from testing was based on a membrane on a bare tube. Thus no long-term data with a carbon-aided tube was collected on long term. In routine handling a carbon-aided membrane tube, we dropped it. A small, but noticeable, quantity of carbon issued from the tube leading to suspicion about the mechanical integrity of the carbon layer. We tested the tube and found its performance to be unimpaired. The feeling was (1) that the bare tube had yielded substantially equal performance to the ceramic tubes, especially for rejection of organics, (2) that the potential benefit of carbon additive was small, and (3) that the mechanical reliability of the membrane was less by some small, unestimated amount. Therefore we concluded at that time, and until a reliability comparison under mechanical vibration conditions could be conducted, that the gains were too small to justify the risk.

Table 1. MEMBRANES FORMED ON STAINLESS STEEL SUBSTRATES

Tube	Material	Diameter (mm)	Pore Size (microns)	Flux (m/sec)	Rejection (%)	Remarks ^a
1	SS	6.0	0.20	2.60 (-5)	66.0	Formation in chlorides
1	SS	6.0	0.20	2.60 (-5)	72.0	Regeneration
2	SS	6.0	0.50	1.30 (-5)	60.0	-
-	ceramic	-	0.27	3.00 (-5)	77.0	-
3	SS	6.0	0.50	2.20 (-5)	77.0	-
-	ceramic	-	0.27	3.80 (-5)	77.0	-
3	SS	6.0	0.50	2.70 (-5)	84.0	After regeneration
4	SS	6.0	0.50	4.90 (-5)	56.0	-
-	ceramic	-	0.27	6.10 (-5)	56.0	-
4	SS	6.0	0.50	4.40 (-5)	71.0	After regeneration
-	ceramic	-	0.27	6.10 (-5)	79.0	After regeneration
5	SS	3.0	0.50	3.60 (-5)	52.0	Unusual rejection vs pH
-	ceramic	-	0.27	5.50 (-5)	77.5	behavior
6	SS	3.0	0.50	10.00 (-5)	32.0	Unusual rejection vs pH
-	ceramic	-	0.27	6.00 (-5)	86.0	behavior
7	SS	2.0	0.20	0.10 (-5)	50.0	-
8	SS	2.0	0.20	0.10 (-5)	48.0	-
-	ceramic	-	0.27	-	72.0	-
9	SS	2.0	0.20	0.60 (-5)	75.0	-
10	SS	2.0	0.20	1.80 (-5)	74.0	-
9	SS	2.0	0.20	0.10 (-5)	89.6	After regeneration
10	SS	2.0	0.20	0.40 (-5)	92.2	After regeneration
11	SS	12.5	0.20	0.20 (-5)	-	-
12	SS	2.0	0.20	0.05 (-5)	68.0	-
13	SS	2.0	0.20	0.17 (-5)	78.0	-

Table 1. (continued)

Tube	Material	Diameter (mm)	Pore Size (microns)	Flux (m/sec)	Rejection (%)	Remarks ^a
-	ceramic	-	0.27	0.48 (-5)	85.0	-
12	SS	2.0	0.20	0.20 (-5)	48.0	Tubes cleaned and reformed using carbon filter aid
13	SS	2.0	0.20	0.30 (-5)	46.0	
-	ceramic	-	0.27	1.80 (-5)	82.0	-
Experience from Different Project						
14	SS	12.5	0.20	1.00 (-5)	-	-
15	SS	12.5	0.50	2.60 (-5)	77.0	-
16	SS	12.5	0.50	1.40 (-5)	73.0	-
17	SS	12.5	0.50	2.30 (-5)	60.0	-
18	SS	12.5	0.50	2.00 (-5)	24.0	-
19	SS	12.5	0.20	0.20 (-5)	42.0	Carbon filter aid
20	SS	12.5	0.50	2.60 (-5)	82.0	Carbon filter aid
21	SS	12.5	0.50	1.70 (-5)	89.0	Carbon filter aid

^a Formed in nitrate solution except as noted; no filter aid except as noted.

3.2 NINETY-DAY TEST RESULTS

3.2.1 Objective and Test Description

An extended test was run to define the flux/time characteristics of the dynamic, zirconium oxide polyacrylic acid (ZOPA) membrane. Observations of the independent effects of temperature, velocity, pressure, concentration, and feed acidity were conducted.

The test was performed on the flow system described in Appendix A. In brief, that system is of 300 series stainless steel material, with seals and fluid couplings of teflon, natural rubber, viton, ethylene propylene, carbon, and tungsten carbide. Membranes were formed according to either prescription 1 or 2, with the second replacing the chloride ion of the first by a nitrate ion as shown in Table 2. After formation, the membranes were stored in water and upon assembly of the selected membranes, a PAA layer was regenerated prior to test commencement. The membranes selected were #13, #16, #31, and #34S having characteristics shown in Table 3.

The annular flow configurations for the ceramic membrane support tubes were developed especially for this test. Figure 1 shows the support arrangement as finally evolved. The average ceramic tube, of diameter 0.53 cm (0.21 inch), was placed in a thick-walled 3/8 inch tubing having an I.D. of 0.622 cm (0.245 inch). One end of the ceramic tube was sealed by the manufacturer using a glass bead and the end was not modified. The other end was open and seated into a recess providing an O-ring which prevented concentrate from leaking into the filtrate flow. The glass bead end was cradled by an extended rod drilled to receive the end. In one case tested, this cradle was omitted with no observed effect. Both ends of the tube were cushioned to preclude metal contact. No cases of tube failure were observed due to pressurization. However, neither the tubes nor the surrounding tubular holder was perfectly straight, leading to physical contact of the support with the holder in several cases. One holder was not usable due to misalignment, and several ceramic tubes were too crooked to allow installation. Several tubes were broken during installation/removal.

Table 2. MEMBRANE FORMATION PROCEDURE

System Cleaning:

Hot phosphate wash (optional), drain, and rinse.
1 molar nitric acid wash for one hour at 50°C. Drain and rinse.
1 molar sodium hydroxide wash for one hour, cold.
Repeat acid and base wash if bubbles occur. Drain and rinse.

During cleaning, all passages must be subjected to circulation of fluid. Stainless steel tubes must be cleaned in nitric acid prior to formation; ceramic tubes require no cleaning.

Formation of Zirconium Layer:

Fill with distilled water or equivalent.

Prescription #1 - Chloride

Add 0.04 - 0.05 molar NaCl
Add 1×10^{-4} molar $ZrO_2Cl \cdot 8H_2O$

Prescription #2 - Nitrate

Add 0.04 - 0.05 molar $NaNO_3$
Add 0.04 g/l $ZrO \cdot NO_3 \cdot nH_2O$

Circulate the solution at 20 - 45°C past the membrane support tube at 5 to 10 m/sec, raising the pressure to 6.5×10^6 N/m² as soon as practical. A flux decrease to 2×10^{-4} m/sec or below indicates the membrane has formed.

Add acid to lower the pH to 2.0; for prescription #1 add HCl; for prescription #2 add HNO_3 . Add 50 mg/l PAA (we use Rhom and Haas Acrysol, 25% solution, A-1 or A-3). In half-hour increments, raise the pH in units (2 to 3, 3 to 4, etc.) to neutralize the solution using NaOH. The acid excursion may be repeated for some improvement in performance.

Regeneration consists of a low pH excursion with salt (NaCl or $NaNO_3$) and PAA as the constituents. The PAA amount may be less than 50 mg/l or even zero. The process is beneficial in restoring performance sometimes lost during storage.

Table 3. MEMBRANES SELECTED FOR TESTING

	<u>Membrane</u>			
	#13	#16	#31	#34S
Date formed	3/24/75	3/28/75	6/9/75	6/18/75
Date regenerated	7/11/75	7/11/75	7/11/75	7/11/75
Flux(1) at formation (m/sec)	7.3×10^{-5}	5.0×10^{-5}	7.7×10^{-5}	3.5×10^{-5}
% rejection(2) at formation (pH)	92.6 (6.7)	92.8 (6.4)	91.6 (6.8)	83.5 (7.5)
Flux(1) after regeneration (m/sec)	5.3×10^{-5}	4.8×10^{-5}	8.8×10^{-5}	(3)
% rejection after regeneration	91.9	89.3	94.1	(3)
Nitrate or chloride	chloride	chloride	nitrate	nitrate
Ceramic or steel	ceramic	ceramic	ceramic	steel

(1) Fluxes correct to 71.8°C by

$$\phi/\phi_0 = e^{-2540 \left(\frac{1}{T} - \frac{1}{T_0} \right)}$$

ϕ = flux at observed temperature T

ϕ_0 = standard flux at $T_0 = 345^\circ\text{K}$

(2) Rejection is conductivity rejection from 0.05 molar salt solution at the observed pH condition indicated in parenthesis. Some variation with pH is expected.

(3) Data were not taken for the steel tube due to the relatively long flow transient.

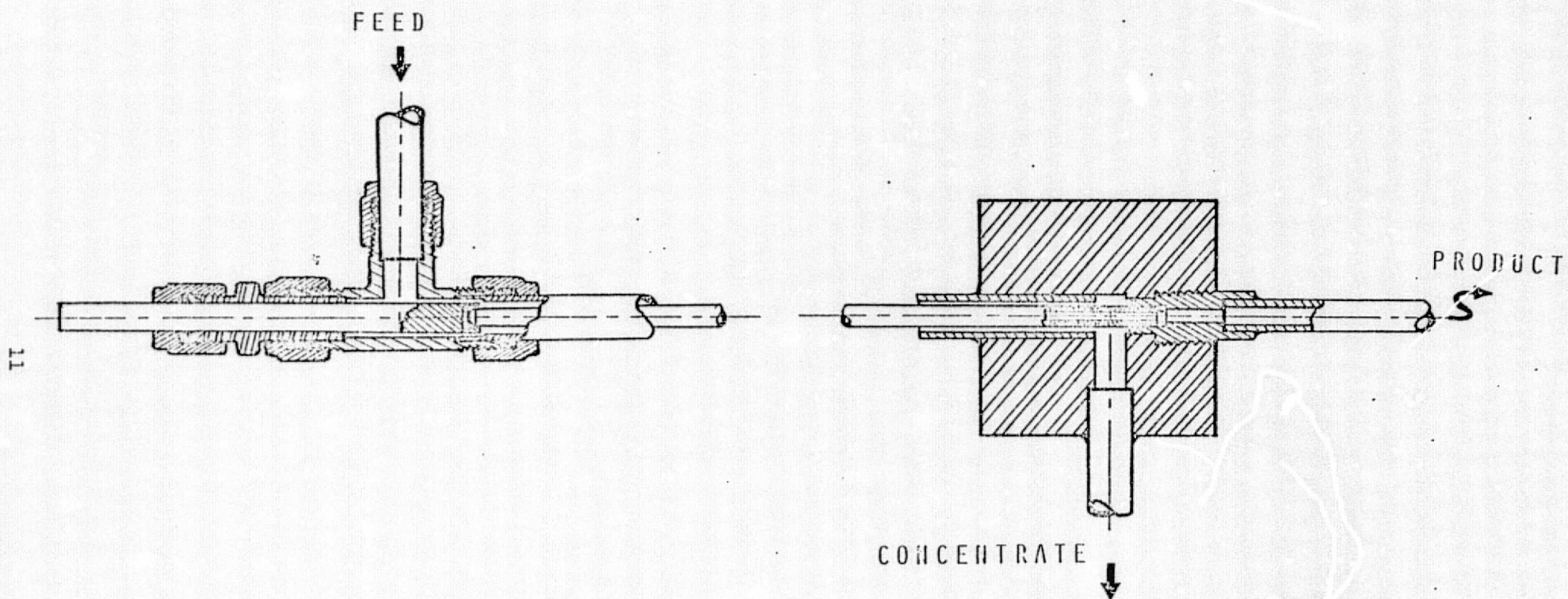


FIGURE 1 ARRANGEMENT OF ANNULAR FLOW BETWEEN A TUBE AND A CERAMIC MEMBRANE SUPPORT TUBE.

The stainless steel tubes were mounted in a holder supplied by the manufacturer. Figure 2 shows the holder details. As is the case with every inside-pressurized tube, the volume of the filtrate chamber is quite large, leading to slow response of filtrate concentration. The tube itself was a 0.5 micron (manufacturer's rating) pore size tube of 316L stainless steel sintered particles.

3.2.2 Experimental Procedure

It was anticipated that operating velocity would have a pronounced effect on the flux decline and perhaps on rejection. Experience suggested that flux declines would be well manifested within 200 hours, since the greatest change generally occurs on fresh exposure to waste. Therefore, in about 200-hour intervals the membranes were scheduled for reductions in operating velocity, with one (#16) to remain at a high velocity as a type of control.

Variations in operating temperature were permitted during the test, and the membrane flux variations recorded. Operation from 68 to 90°C was observed. A temperature scan from 52 to 95°C was conducted near the end of testing to record parametric effects. The pressure was maintained at $6.9 \times 10^6 \text{ N/m}^2$ (1000 psi) for all except a brief period wherein the pressure parametric effect was noted.

It was impossible to expose the membranes to actual prototype concentration-time conditions due to the nature of the flow setup. However, concentrations varying from feed to 30x volume concentrations were imposed. A feed batch was allowed to be processed while the filtrate was either recirculated or withdrawn. Withdrawal of filtrate was equivalent to the concentration elevation produced within the long filter passages of the expected prototype. Each batch of waste was concentrated thusly until the loop's minimum volume was reached.

The amount of fresh wash water produced for processing was calculated to simulate the loading expected for flight application. In ninety days, one shower per day per man of a six-man crew will generate 540 man-showers. These 540 man-showers will be processed by an expected 200 tubes for an average loading of 2.7 man-showers per tube. In the laboratory element test, four tubes processed 36 man-showers for an average of 9 man-showers per tube. The total area exposed was 282 cm^2 for an average 0.128 man-showers per cm^2 . Two hundred tubes, 1.5 mm in diameter and 30.5 cm long, represent 2870 cm^2 (this is the expected size of the smallest manufacturable membrane). With the test loading of 0.128 man-showers per cm^2 , the 2870 cm^2 membrane would be exposed to 367 man-showers, or about 70% of the expected flight loading. It is felt that the test loading in man-showers per unit area reasonably well simulates the expected conditions even for the smallest projected membrane.

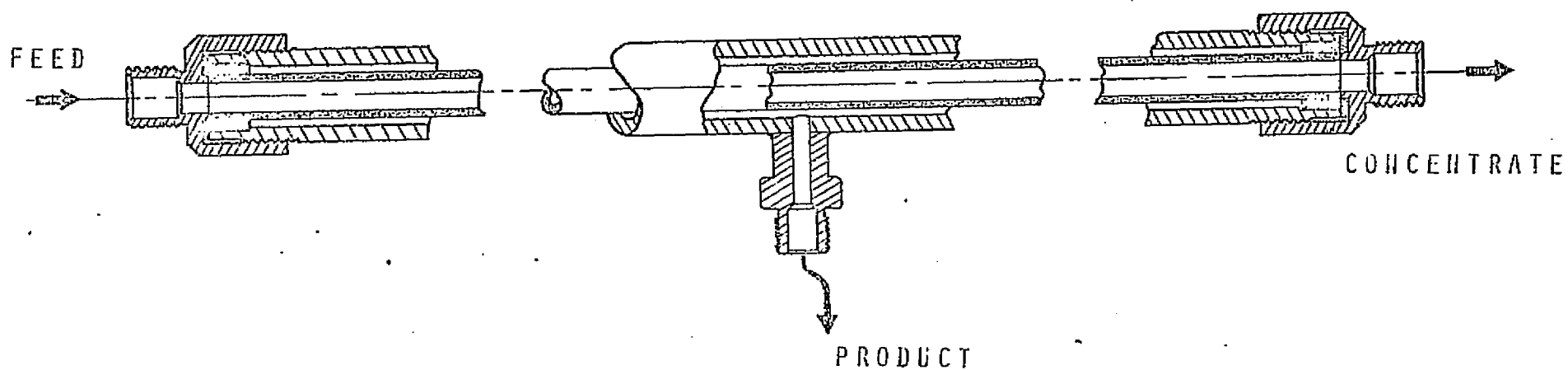


FIGURE 2 ARRANGEMENT OF INSIDE-PRESSURIZED STAINLESS STEEL MEMBRANE SUPPORT TUBE

Wash water was generated according to a modification of the prescription in Reference 8. Based upon the experience reported in Reference 6, the additional makeup chemicals used in the prescription were suspected of causing an unduly acid wash water (pH below 5). Work in progress at that time (reported in Reference 9) also suggested that shower water was lower in solids than as characterized in Reference 8, alleviating the need to supplement the feed. The major modification to the generated wash water then was the deletion of additive solution except for makeup urea which will be addressed later. Other modifications were in dress of subjects, amounts of soap, and particulate filtration. The subjects usually showered in late afternoon and would exchange outer clothing for exercise clothing, retaining inner wear. The inner garments would be laundered with the exercise shorts and towel. It is felt that this procedure more nearly simulated actual body solid carryover than the donning of a special exercise suit including inner wear. All subjects were allowed to use as much cleansing agent as desired. Actual usages were recorded. Filtration was through a single, 20-micron cellulose acetate cartridge filter except for trials with a piece of towelling and a small patch of porous nylon filter material.

During the course of testing, it was noticed that there was a decrease in the urea content and in total nitrogen of the feed. The hydrolysis of urea to carbon dioxide and ammonium and ammonia is expected at the temperature levels of the testing. Attempts to seal the system to prevent the escape of ammonia were not successful. Primitive calculations showed that the gas void in the feed reservoir could, at saturation, contain relatively large quantities of ammonia so that sealing would be ineffective. Therefore at approximately daily intervals, the solution was enriched by approximately one-half gram of urea. This action restored the exposure of the membrane to urea and ammonia to some extent, and permitted more accurate analysis of the urea filtration effectiveness (rejection). The latter analysis is less accurate at low urea levels.

During a running day, the loop was started and observed until it became reasonably stable. All corrections to pressure, velocity, and temperature were made and the loop allowed to operate for two to five hours. Then, the product in the return lines between the module and reservoir was drained as the sample for the day. Fresh product was then collected for a flow rate determination. Samples sent to NASA-JSC were refrigerated until they could be inserted into special boxes containing dry ice for cold shipment. Samples to be analyzed for ammonia and urea were cooled to room temperature $\pm 1^\circ\text{C}$ before analysis; conductivity and pH were measured hot. Measurements were made with the following list of instruments:

<u>Item</u>	<u>Device</u>	<u>Calibration, Expected Accuracy</u>
Temperature (beaker)	Mercury thermometer	None, 1°C.
Temperature (flow)	Cu Cn thermocouple	1974. Checked periodically with thermometer, 1°C.
Pressure	Bourdon tube	1974. 1×10^5 kg/m ² (12 psi).
Flow	50 ml cylinder	None, 0.5 ml \rightarrow $\pm 5\%$ accurate at usual volume levels.
Velocity	Rotameter	None, \rightarrow ± 0.15 m/sec
pH	Fisher Model 330	Routine calibration with buffer solutions.
Conductivity	Balsbaugh Model 100	Calibrated on standard solution.
Ammonia, urea	Orion NH ₃ probe	About a weekly calibration and a daily check. One mv accuracy. About $\pm 10\%$ accuracy on NH ₃ content.

3.2.3 Results

The major events during testing are listed in Table 4, which indicates the elapsed time at which feed was added, the velocity setting, and the times at which the loop was rinsed. These major event headings are indicated on most of the performance versus time charts as dashed lines.

The concentrate solution properties pH and electrical conductivity are shown in Figure 3 as a function of time during the test. A general trend is prevalent during each fluid batch history. Fresh feed is slightly acid but as the urea decomposes, it becomes more alkaline. Then, as the concentration rises (indicated by conductivity increase), the acidity again decreases. This is probably due to the relatively greater rejection of lactic acid compared to ammonium causing the acid to be preferentially concentrated in the circulating solution. This action is similarly expected in a prototype situation, wherein the highly concentrated, exit-end fluid will display a lower pH. Also the prototype case will not provide as much time for reactions to increase the pH as occurred in the laboratory test. The relatively high observed pH of the product water should not be manifest in the

Table 4. EVENT LISTING

Event #	Time (hr)	Number of Man-showers	Velocity (m/sec)	Temperature Range, °C	Comments
1	0 - 142	5	#13 - 3.9 #16 - 3.9 #31 - 3.9	68 - 82	81ℓ of filtered shower water
	142				20ℓ of filtered feed collected, system rinsed
2	150 - 310	6	#13 - 1.8 #16 - 1.8 #31 - 1.8 #34S- 1.4	79 - 83	111ℓ of filtered feed collected (foaming towards end)
3	310 - 515		#13 - 1.8 #16 - 1.8 #31 - 1.8 #34S- 1.4	73 - 82	20ℓ of concentrated feed from 142 hours added to feed in loop, 15ℓ of feed collected and system rinsed
4	533 - 773	6	#13 - 1.0 #16 - 1.9, 1.4 #31 - 1.0 #34S- 1.9, 1.4	75 - 80	114.5ℓ of filtered shower water
	774				feed dumped, pump checked, system is not rinsed
5	775 - 1110	5	#13 - 1.0 #16 - 1.8, 1.4 #31 - 1.0 #34S- 1.8, 1.4	76 - 85	92.5ℓ of filtered shower water
6	1110 - 1133		#13 - 1.0 #16 - 1.8, 1.4 #31 - 1.0 #34S- 1.8, 1.4	74	same feed as #5 but in internal loop flow
7	1133 - 1416	3	#13 - 0.3 #16 - 1.9 #31 - 0.3 #34S- 0.8	72 - 77	add 53.5ℓ of filtered shower water to above feed

Table 4. (continued)

Event #	Time (hr)	Number of Man-showers	Velocity (m/sec)	Temperature Range, °C	Comments
8	1416 - 1475		#13 - 0.3 #16 - 1.9 #31 - 0.3 #34S- 0.8		same feed as #7 but in internal loop flow
9	1479 - 1824	4	#13 - 0.16 #16 - 1.9 #31 - 0.16 #34S- 0.5	69 - 73	add 74% of filter- ed shower water to the above feed
10	1825 - 2048 2048	3	#13 - 0.16 #16 - 1.9 #31 - 0.16 #34S- 0.5	71 - 90	add 55.5% of filtered shower water to the above feed collected 16% of concentrated feed and rinsed loop
11	2066 - 2088	2	velocity	temperature	add 37% of filter- ed shower water
12	2088 - 2172	2	profile	profile	add 37% more of filtered shower water

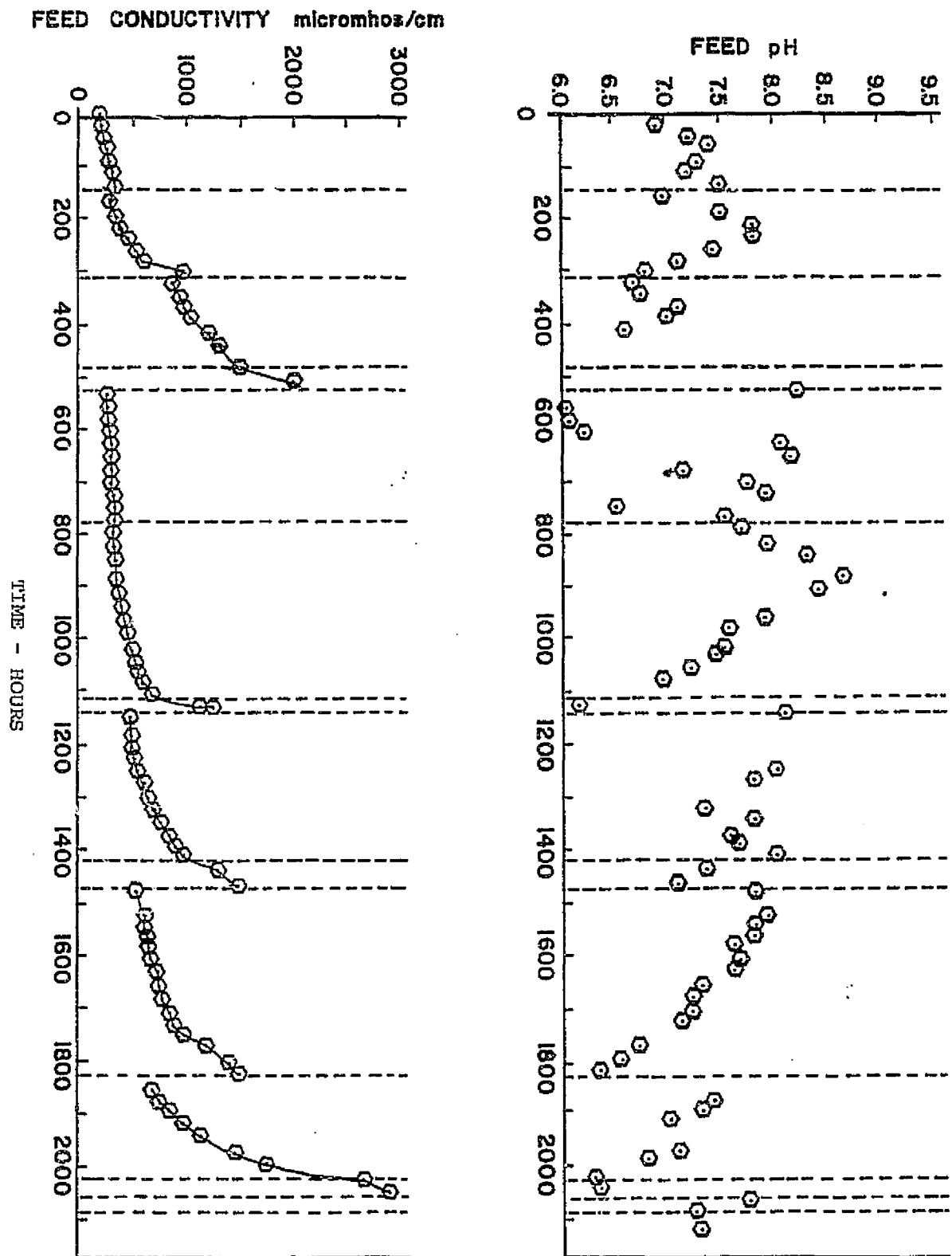


Figure 3. Time variation of feed solution pH and conductivity.

prototype situation. Nor should the pH be expected to drop much below 6.0 for the concentrate flow.

The resulting membrane flux and conductivity rejections are shown in Figure 4. Since the flux depends so strongly upon temperature in a predictable way, the fluxes have been corrected according to the relation

$$\phi = \phi_0 \exp \left(-2540 \left[\frac{1}{T} - \frac{1}{T_0} \right] \right)$$

Here ϕ is the measured flux at temperature T , and ϕ_0 is the corrected flux at temperature $T_0 = 350^\circ\text{K}$. The initial fluxes on waste compare to the earlier measured value on salt solution as shown below.

Membrane	Flux Before Waste	Initial Flux on Waste	% Change
#13	5.3×10^{-5}	3.1×10^{-5}	-41
#16	4.8×10^{-5}	5.5×10^{-5}	+14
#31	8.8×10^{-5}	5.3×10^{-5}	-39
#34S	3.6×10^{-5a}	1.8×10^{-5}	-50

^a Before regeneration.

Three membranes displayed 40 - 50% flux declines immediately, agreeing with previous experience. Membrane #16 registered an increase and as shown in Figure 4 the product flow varied considerably for several days then stabilized into a slow decline. During this initial period the rejections were uniformly high and began a slow decline. Fluxes of all membranes, shocked by exposure to waste, had begun a noticeable upturn by the 140-hour point.

At 142 hours a system rinse was performed and a fresh batch of shower water added. This rinse did nothing to increase performance; rather, declines in both flux and rejection were registered with the second feed addition. Exposure to the second fresh waste caused an immediate decline in flux to below the lowest level observed during the first batch. Operation was virtually steady except for a significant drop in flux for tubes #16 and #34S from 400 to 510 hours. All membranes except for #31 registered a decrease in rejection steadily as the fluid concentration increased.

The third new waste batch was added at 533 hours without a system rinse. This new waste seemed to "clean" the membrane as judged by the trend to higher fluxes in the period 533 to 800 hours. Also, the previously depressed rejections jumped while the unaffected tube #31 dropped but began a recovery. The velocity at 533 hours was changed to 1 m/sec for tubes #13 and #31 while #16 and #34S were maintained at 1.8 and 1.4 m/sec, respectively. The rejections were affected by the velocity, pH, and concentration changes at the same time.

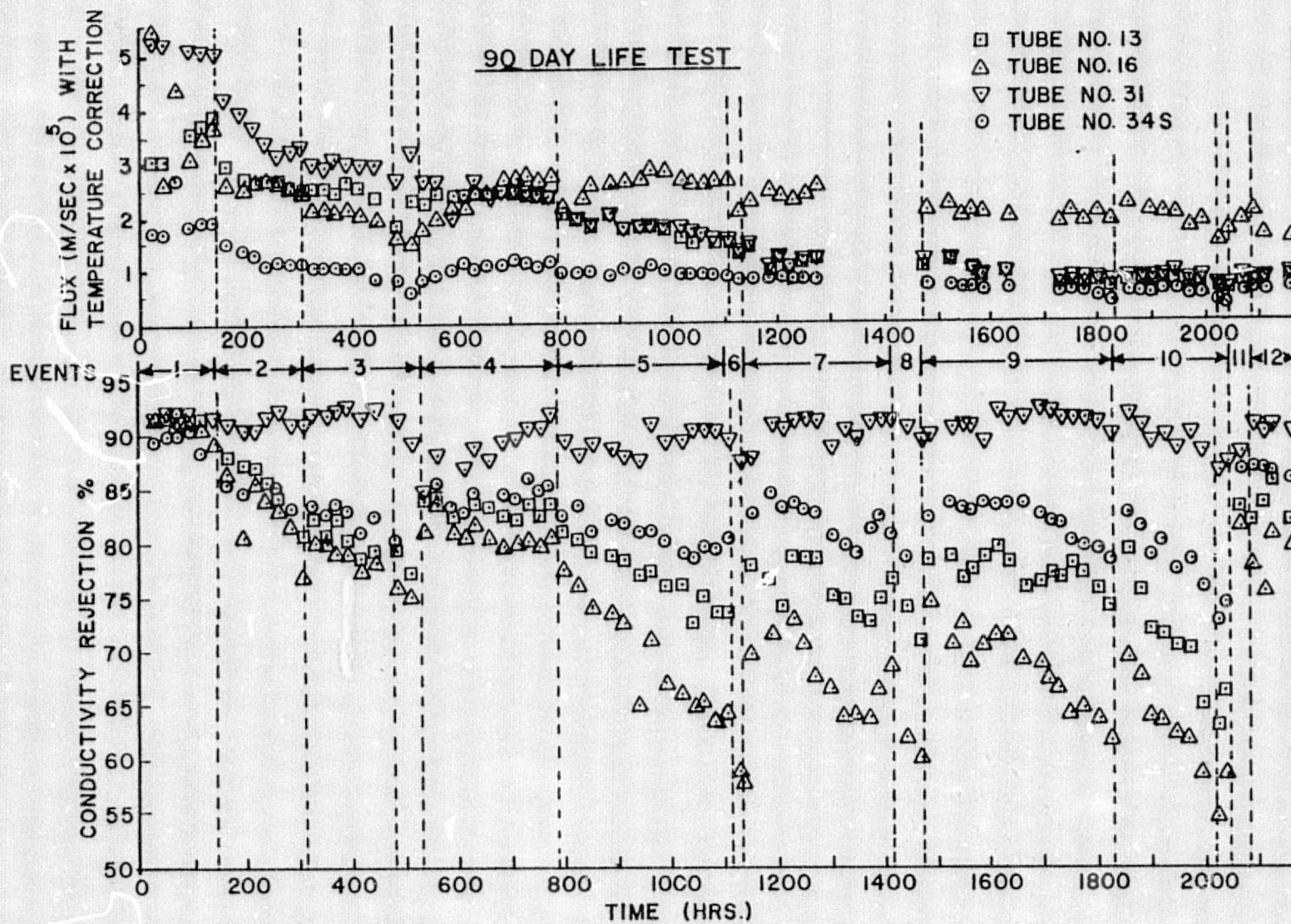


Figure 4. Performance data for ninety-day test.

Beginning at 533 hours, a pattern emerged which appears to be characteristic of the "mature" membrane. Tube #31 maintained a uniformly high rejection even at extremely low velocities, while tube #16 maintained the lowest rejection even though it was not subjected to low velocity operation. Not only was the rejection lower for tube #16 but the influence of concentration was extremely more pronounced. The stainless steel tube #34S meanwhile had achieved second position in rejection which it maintained from then on though it was poorest at formation. Tube #13 was operated as nearly identical to tube #31 as was possible; however, the performance in no way was related as regards the rejection.

Beginning at 533 hours, the flux characteristics also began a somewhat systematic pattern. Beginning at this time tubes #13 and #31 exhibited nearly identical flux behavior, declining more or less steadily from 2.6×10^{-5} m/sec to a low of 0.6×10^{-6} m/sec. During this period, tube #16 registered an increase in flux which was depressed somewhat upon new feed additions and which was fully manifested by 1000 hours. Flux of tube #16 thereafter followed a general decline. This entire event saw the flux rise from 1.8×10^{-5} m/sec to a high of 2.9×10^{-5} m/sec and to a low of 1.6×10^{-5} m/sec. Meanwhile, the steel tube #34S also observed a rise in flux from 0.9×10^{-5} to 1.2×10^{-5} m/sec followed by a decrease to 0.4×10^{-5} m/sec.

A water rinse at 2048 hours restored both flux and rejection. The flux increase registered was 10% for tube #16, 22% for tube #13, 26% for tube #31, and 54% for tube #34S. Except for the brief, reversible (by washing) low flux periods, tube #34S displayed the most consistent flux performance at a max/min ratio of 1.5 from 250 hours to the end of the test. By the same evaluation rules of omitting the brief excursions, tube #16 exhibited an extreme ratio of 1.6, tubes #13 and #31 showed a ratio of 2.8 from about 600 hours onward.

The maximum to minimum flow ratio is important in connection with control of pressure and flows of the prototype hardware. A low ratio greatly simplifies the control situation and probably, depending on the control used, will allow a reduced power penalty.

The rinse and addition of fresh waste at 530 hours and no rinse with fresh waste at 1824 hours were also effective in increasing flux. The table below compares the flux increase due to the fluid change at 530 hours, 1824 hours, and 2048 hours.

<u>Flux Changes</u>					
<u>Event</u>	<u>Time</u>	<u>Tube #13</u>	<u>Tube #16</u>	<u>Tube #31</u>	<u>Tube #34S</u>
Rinse and new feed	530	+13%	+86%	0 or negative	+100%
New feed	1824	+33%	+10%	+ 6%	+ 33%
Rinse and new feed	2048	+22%	+10%	+26%	+ 54%

By the same token, feed additions at 775 hours, 1133 hours, and 1480 hours did not produce any apparent systematic flux recoveries. The main statement applicable to this observation is that whenever the membrane flux is relatively lowered by the feed (e.g., at 530, 1824, 2048 hours) a flux recovery is expected; while in cases (775, 1133, 1480 hours) where the flux has not been relatively lowered, no recovery occurs. A tabulation of fluxes after feed addition is shown below.

Time	$10^5 \times \text{Fluxes}$ (m/sec)			
	Tube #13	Tube #16	Tube #31	Tube #34S
530	2.2	1.8	2.70	0.85
775	2.0	2.2	2.20	0.95
1133	1.4	2.3	1.50	0.90
1480	1.1	2.2	1.20	0.80
1824	0.8	2.2	0.90	0.60
2048	0.9	2.0	0.95	0.60

Both tubes #16 and #34S show fairly stable operation while the tubes #13 and #31 show much more flux variation. During the period prior to 1480 hours, membrane #34S was operated at 0.8 m/sec or greater and it showed a negligible flux decline from 530 hours to 1480 hours. At 1480 hours, the velocity for tube #34S was lowered to 0.5 m/sec and the flux became more erratic. The comparative flux stability of tube #16 compared to tubes #13 and #31 and is considered due to its being operated at a constant 1.8 m/sec velocity compared with the variable velocity of the others, which decreased to 0.16 at 1480 hours. No really definite flux decline versus time relationship can be determined.

The flux data can be plotted on a log plot as in Figure 5. The arrows thereon indicate the events of fresh waste addition and system rinses. All tubes were operated from 0 to 142 hours at a velocity approaching 4 m/sec and showed no flux decline. From 150 to 530 hours, the velocity was 1.4 to 1.8 m/sec and average flux change was significant, declining an average of 40 to 44% over a 380-hour period. These figures are judged from a best fit (by eyeball) straight line fit of the data. The single tube #16 which remained at 1.8 m/sec operation was essentially stable for the remainder of testing. The other tubes were subjected to velocities from 530 hours to 1130 hours of 1.0, 1.0, and 1.4 for tubes #13, #31, and #34S, respectively. Tubes #13 and #34S registered a flux recovery due partly to the rinse but somewhat due to the new feed properties. Tube #31 reacted to the rinse and new fluid with a sudden decrease followed by an increase and a further, sustained degradation in flux. Because of these significant exceptions, no simple flux decline statement is appropriate. One is led to believe, using tube #16 as an example, that the combination of rinse and new fluid would have resulted in an 80% flux increase in

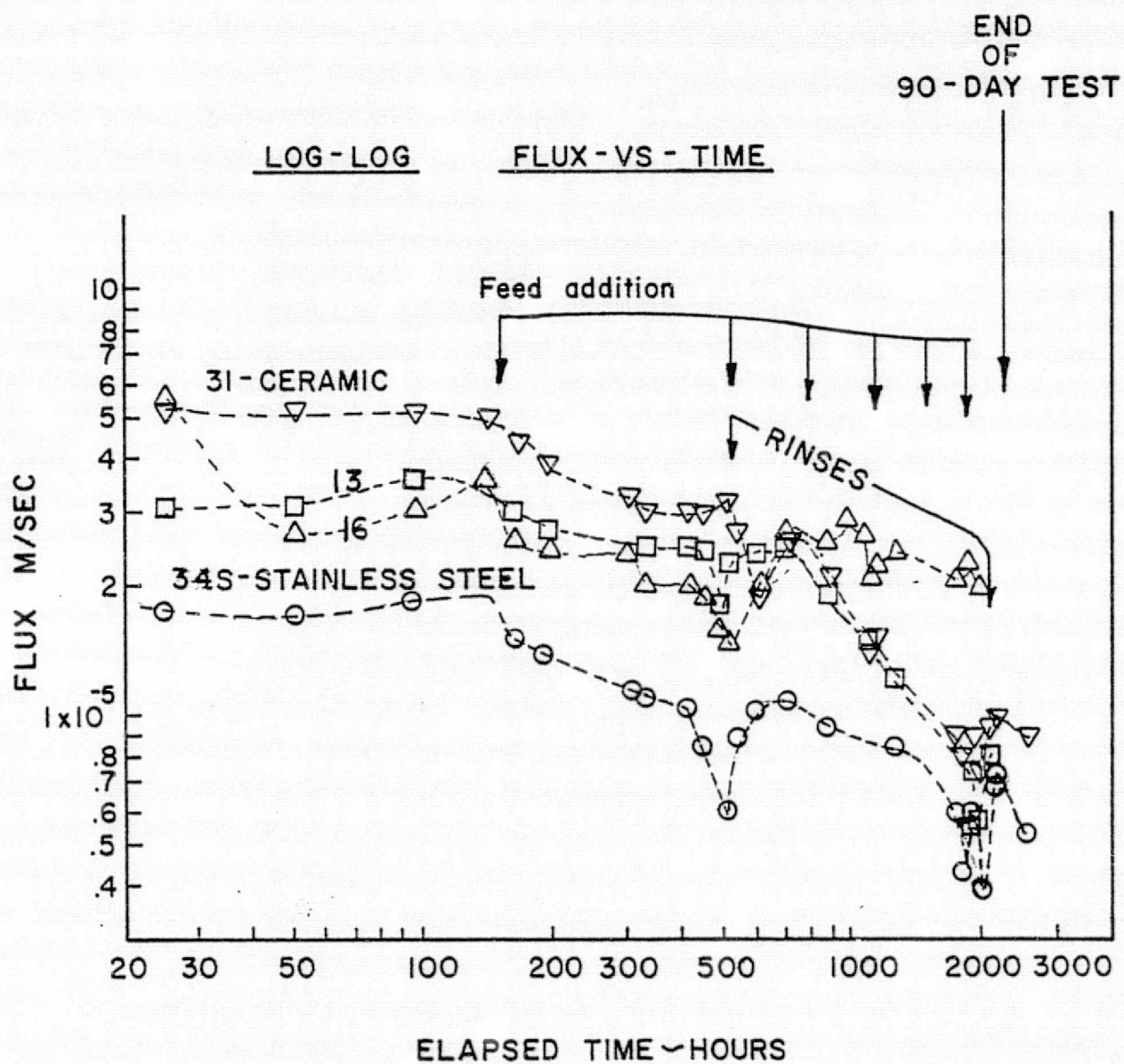


FIGURE 5 LOG FLUX VERSUS LOG TIME

the period from 500 to 700 hours. Using the period from 700 to 1130 hours as that period in which the flux decline is more devoid of otherwise-contrasting influences, one may identify the following "best interpreted" flux declines.

Best Interpreted Flux Declines (430 hours)		
<u>Tube</u>	<u>Velocity (m/sec)</u>	<u>Percentage Decline (700 - 1130 hours)</u>
#13	1.0	44
#16	1.8	0
#31	1.0	44
#34S	1.4	25

From 1130 hours to 1480 hours the velocities were reduced to 0.3, 0.3, and 0.8 m/sec for tubes #13, #31, and #34S, respectively. The percentage decline for the 350-hour period for tubes #13, #16, #31, and #34S were respectively 24%, 15%, 24%, and 13%. The last velocity stage was from 1480 hours to the rinse at 2048 hours and saw velocities reduced to 1.16 m/sec for tubes #13 and #31 and to 0.5 m/sec for tube #34S. During this 570-hour period, fluxes were reduced by 40% for tube #13, 0 for tube #16, 22% for tube #31, and 45% for tube #34S.

If the flux-time relationship is assumed to have the form $\phi \propto t^{-b}$, where ϕ = flux, t = elapsed time from initial exposure, b = flux rate parameter dependent on feed character and velocity of operation, the foregoing best interpretations of data may be used to evaluate the parameter b . The results of such an exercise are plotted in Figure 6 as the value of the parameter b versus the velocity of operation. Some relationship could perhaps be inferred that low velocities tend to increase the value of b indicative of more severe flux decline. However, the plotting of the parameter b versus the feed batch number (from #1 through #4) shown in Figure 7 is perhaps equally meaningful and shows that during the fourth period the decline parameter is virtually the same as in the second period though the velocities were certainly lower. It is believed that no truly systematic variation has been observed of flux versus time.

The variation in conductivity rejection is due to the combined effects of concentration and pH. From Figure 3 it can be observed that a fairly strong correlation between pH and conductivity existed. Because of this correlation, the independent effects of concentration and pH are difficult to discern. In spite of the coupling which exists between the feed pH and concentration, Figure 8 shows the observed variation between rejection and conductivity. For reference, preliminary experiments on salt solution yielded data which were essentially independent of the conductivity of the solution in the range 0 to 3000 $\mu\text{mho/cm}$. Also, our experience has suggested that each membrane

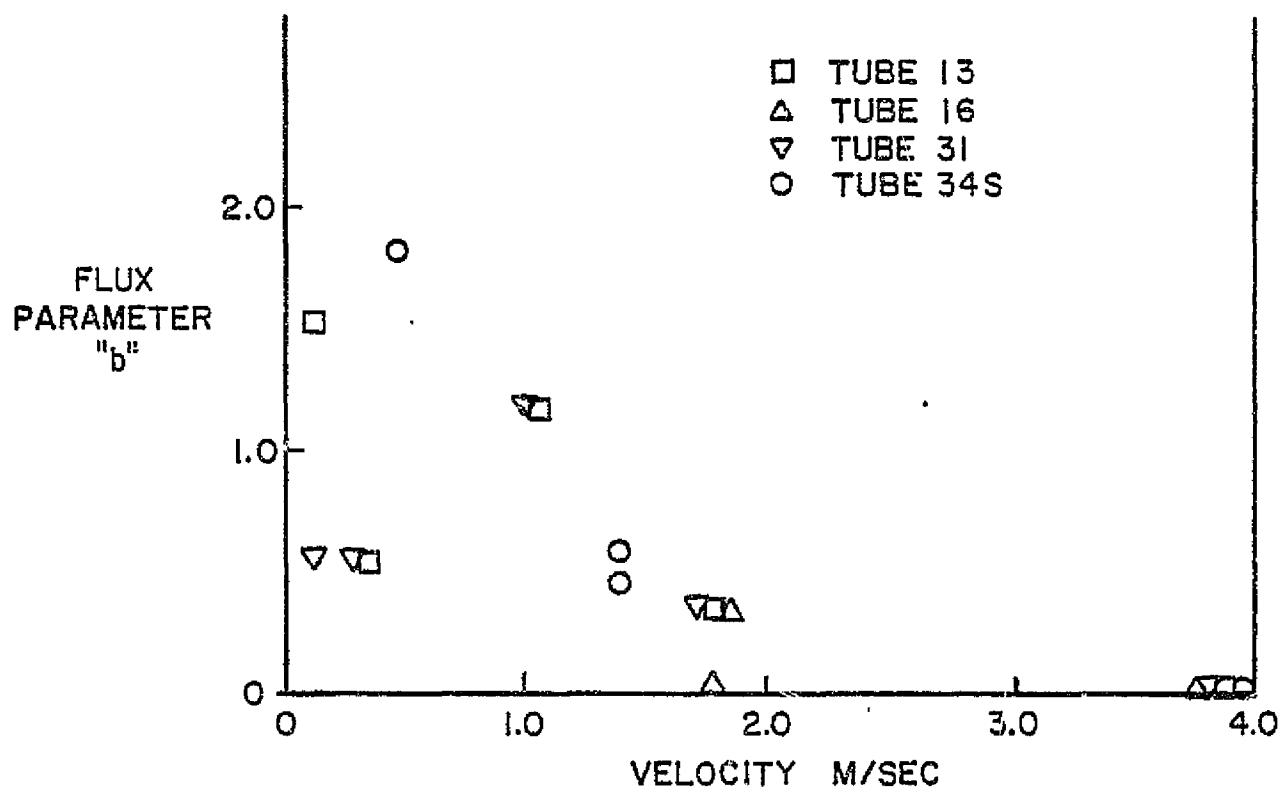


FIGURE 6 FLUX DECLINE PARAMETER OBSERVED
AT SEVERAL VELOCITIES

FLUX
PARAMETER
"b"

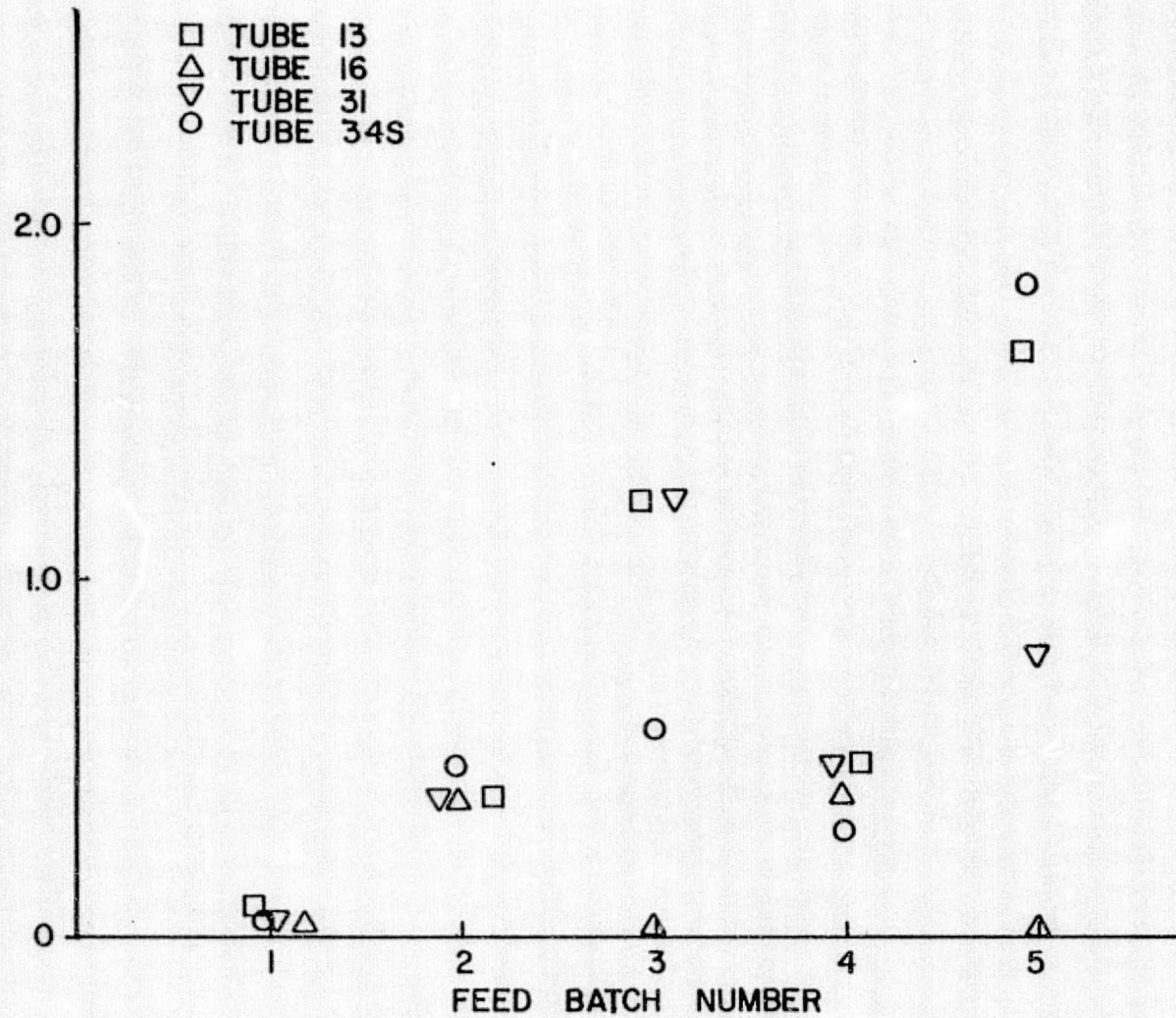


FIGURE 7 FLUX DECLINE PARAMETER OBSERVED
WITH SEVERAL BATCHES

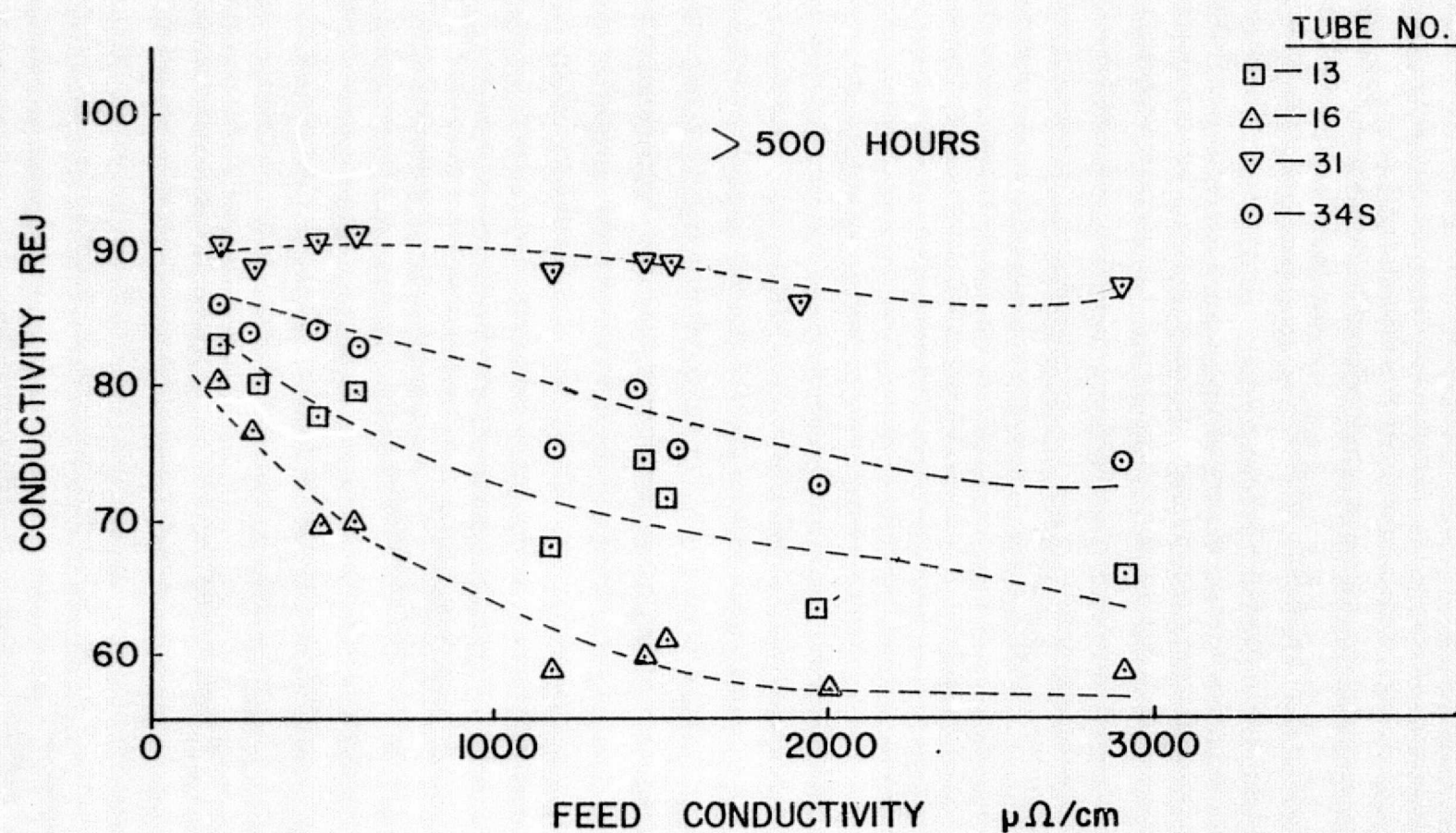


FIGURE 8 EFFECT OF FEED CONDUCTIVITY ON MEMBRANE REJECTION

will exhibit a different response to pH. Judging from experience, the velocity was not responsible for a significant decrease in rejection.

On the whole, the rejection was most affected by tube-to-tube membrane variations which expressed themselves beginning at 100 hours and which were fully evident at about 500 hours. The second most important parameter was concentration and which more greatly affected those tubes having poorer rejection. The effect of pH is perhaps third in importance, but slight in the pH range of interest, in affecting the rejection. The optimum feed pH is between 7 and 8 for conductivity rejection with a loss of 2 to 8% in rejection expected whenever the pH decreases to 6. Finally, the velocity has caused no significant rejection variation during the test. The conjunction of high flux and low velocity has been shown in other tests to produce significant concentration polarization. However, at the fluxes which occurred naturally during the shower water testing, these effects did not reach even predicted levels.

Rejection of other materials not well measured by conductivity are important. The rejection of organic material (TOC) for the early test portions are shown in Figure 9. The principal ingredients in the organic carbon list are the detergent and several body products such as lactic acid. These are filtered rather better than the smaller salt molecules but still with some variation. In fact, a plot (not shown) of organic carbon rejection versus conductivity rejection does display a reasonable correlation.

The average filtrate level of organics is about 20 - 30 mg/l or within the expected minimum TOC requirement of 37 mg/l. Therefore, one-pass filtration is expected to enable the satisfactory depletion of organics in the recycled water. The principal exception to this is urea as considered below.

Urea and ammonia in the filtrate are expected to pose a more difficult problem in filtration. The rejection of ammonia as measured by the specific ion probe at Clemson is shown in Figure 10. Because the ammonia level affects the accuracy of reading, the data in Figure 10 have accuracies estimated within ± 5 percentage points normally. The data taken at Clemson do not compare favorably with those analyzed at Houston. Ammonia depletions of up to 90% during storage and transit are indicated. The filtrate samples are more strongly affected so that the indicated ammonia rejection from samples sent out for analyses is higher by a considerable amount. It is believed, while the specific-ion determination may be less accurate, that the on-site, quick determination of ammonia is required. A direct plot of data from Figures 4 and 10 quickly dissolves any hint of a correlation between ammonia and conductivity rejection. However, if one considers Figure 4 data with the notion that increased

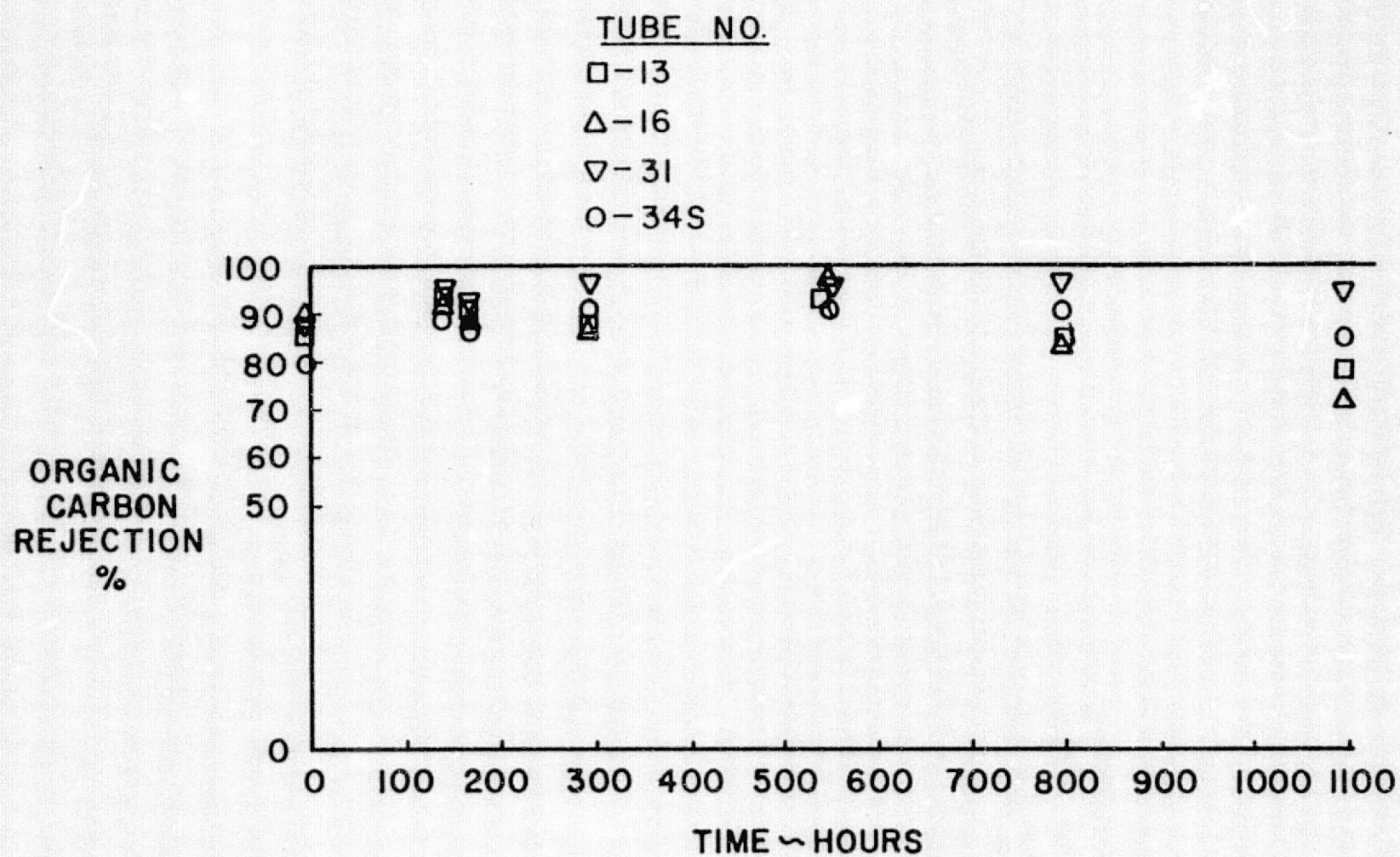


Figure 9. Rejection of organic materials.

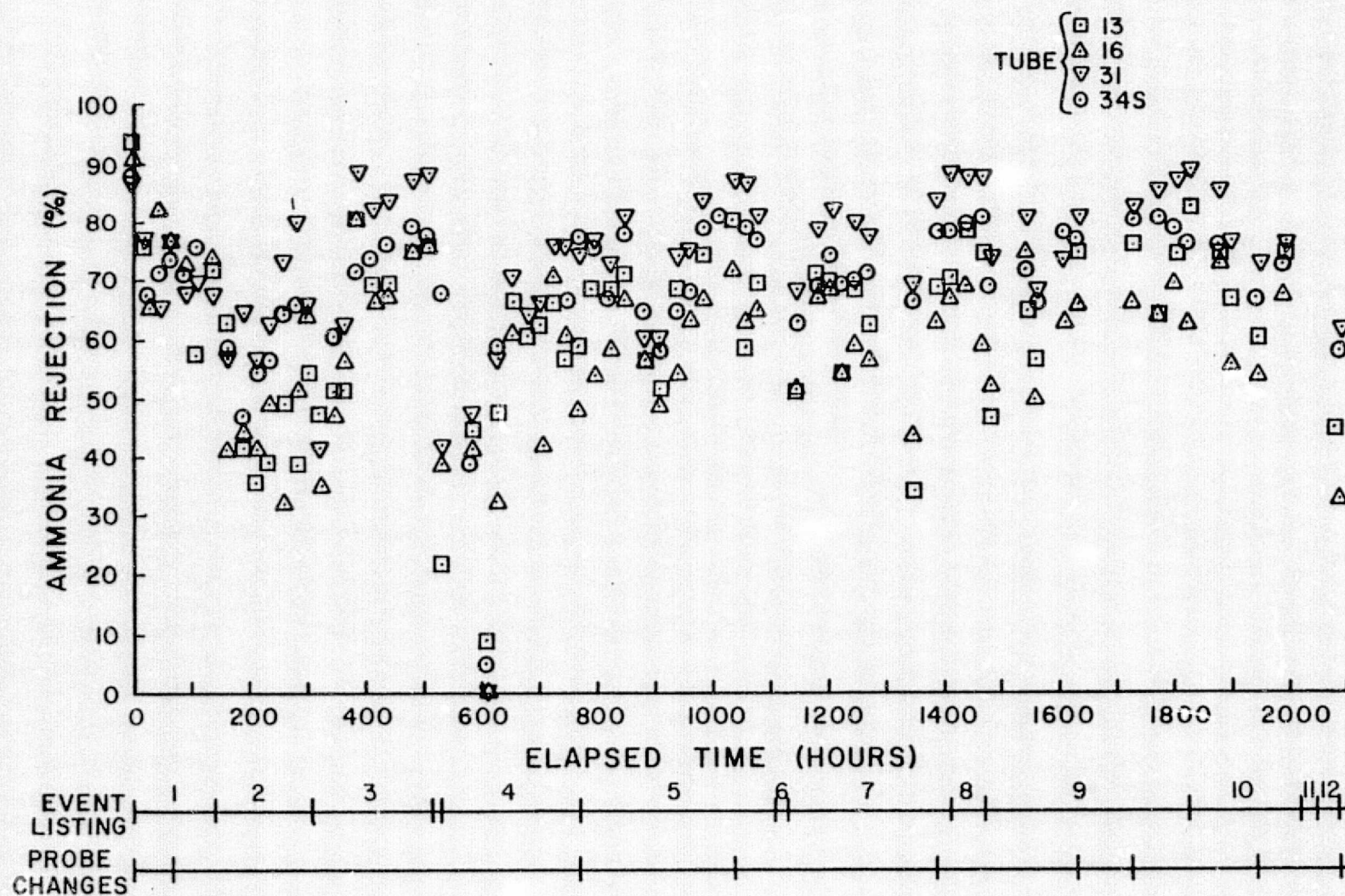


Figure 10. Rejection of ammonia over the test duration.

conductivity tends to reduce rejection of both general salts and ammonia while higher pH might greatly and specifically reduce the rejection of ammonia, one can imagine this resulting in the data of Figure 10. The assumption of lower NH_3 rejection as pH increases from 6 to 7.5 is counter to data for salt, but it is known that the equilibrium between ammonium and ammonia favors the formation of the less rejected ammonia as pH is increased. This is advanced as a possible explanation for the non-correlation of ammonia rejection with conductivity rejection.

Regardless of the details of the ammonia rejection phenomenon, a rejection of something like two-thirds of the ammonia present in wash water may be expected. References 7 and 9 have suggested a feed content of about 25 mg/l so that once-filtered water would still contain 8 mg/l, twice-filtered, 3 mg/l, etc. Thus, twice- or thrice-filtered water will be required to remove the ammonia to the 3 or 1 mg/l projected requirements for wash water or potable water, respectively.

Urea is the primary source of ammonia in the wash water. The makers of standards for water have limited ammonia to low levels while allowing urea levels of 50 mg/l. Hot water (i.e., 74°C) will surely result in hydrolysis of the urea so that the heated water standard for urea should be modified to perhaps 2 - 4 mg/l or that the total N be within some level. The filtration of the small, non-ionic molecule urea is not accomplished efficiently by the ZOPA membrane. Daily data were taken, but no real trend could be proposed considering the inaccuracy of data. However, the means and standard deviations for the membranes are as shown in the following table. Data indicating negative or above 1 have been taken as 0 or 1.

<u>Urea Rejection</u>		
<u>Tube</u>	<u>Mean</u>	<u>Standard Deviation</u>
#13	41	33
#16	41	23
#31	46	21
#34S	40	22

Average mean = 42

At the conclusion of the ninety-day test, further runs were conducted to determine the effect of velocity, pressure, and temperature. The effects of parameters were determined on two fresh wash water batches at essentially no volumetric concentration, between hours 2066 and 2172 (refer to Table 4 and Figure 3). Pressure was varied from $2.6 \times 10^6 \text{ N/m}^2$ to $6.9 \times 10^6 \text{ N/m}^2$. As expected, the flux of product increased linearly with pressure as shown in the upper part of Figure 11. The conductivity rejection as shown in the lower part of

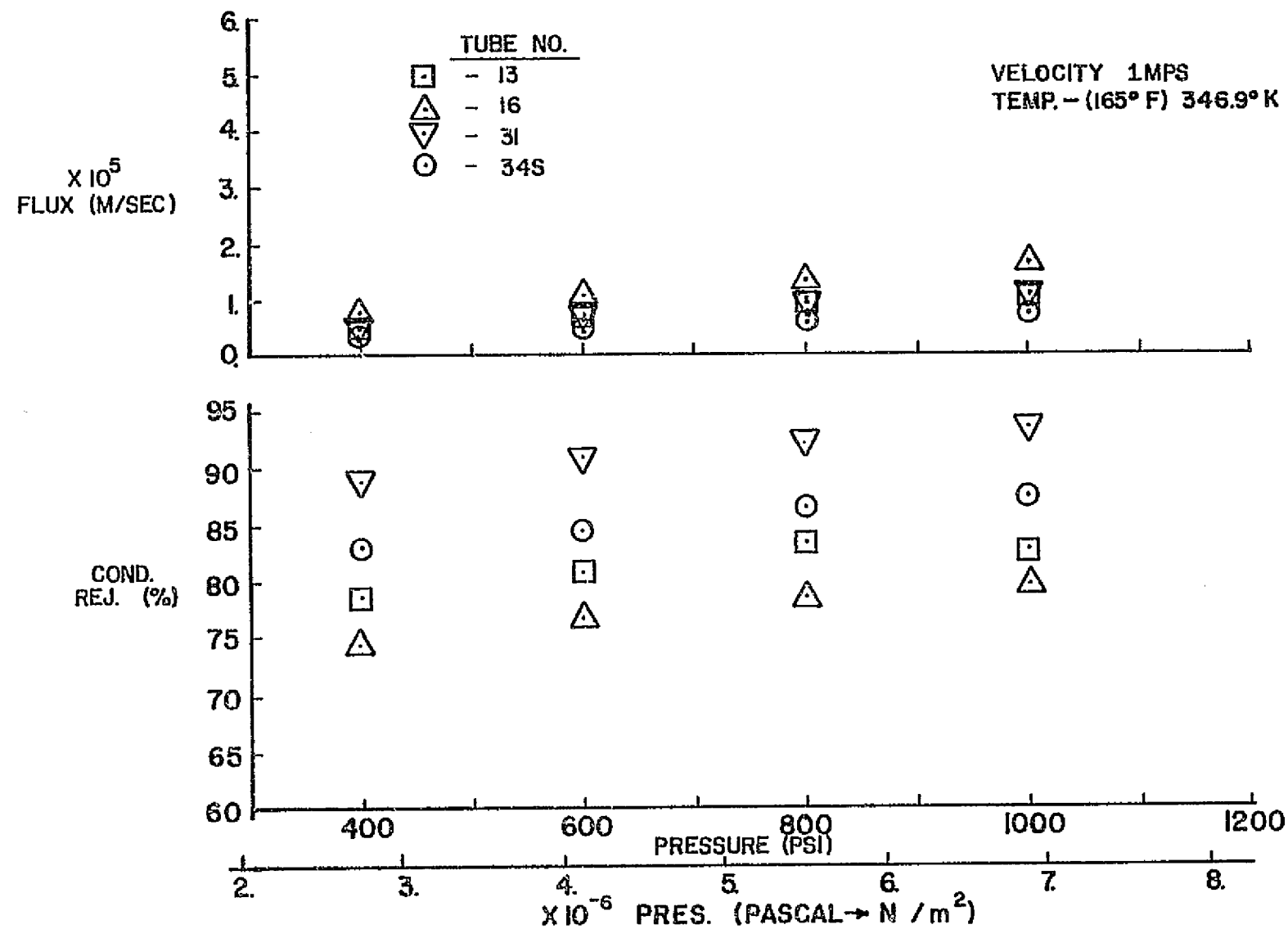


Figure 11. Parametric effect on pressure.

Figure 11 decreased in proportion to the pressure according to a proposed relation

$$1 - \text{rejection} = Ae^{-\gamma P}$$

P is the applied pressure while the values of A and γ are given below which best fit the data of Figure 11.

Tube	A	γ (m ² /N)
#13	0.246	6.250 (-8)
#16	0.286	5.340 (-8)
#31	0.150	1.263 (-7)
#34S	0.209	7.870 (-8)

These relations fit the data to ± 1 percentage point.

A temperature survey was conducted in the temperature range 52 to 95°C. The major effect of temperature on the membrane processes is expressed in the flux which more than doubles in the temperature range tested. Figure 12 displays the data taken for flux and conductivity rejection. The conductivity rejection shows perhaps a slight decline as the temperature is raised. The use of temperature as a means of flux control may prove beneficial in the prototype design. Figure 13 is a semi-logarithmic replot of the temperature data with those from 1974 (Reference 1) shown for comparison. The average value of β is 2540, which has been used to adjust the raw flux data for temperature effects according to the equation

$$\phi = \phi_0 \exp \left(-\beta \left(\frac{1}{T} - \frac{1}{T_0} \right) \right)$$

where ϕ = flux at Temperature T
 ϕ_0 = flux at Temperature T
 β = 2540 (K⁻¹).

A survey of velocity effects is summarized by the data in Figure 14. The data span the anticipated value of transition Reynolds modulus for the ceramic tubes occurring at 1 m/sec, but the steel tube data extend only to a Reynolds number of 9000. Theory predicts a mild rejection jump due to transition but its effect is not strong enough to be apparent in the data of Figure 14. The loss in rejection for tube #16 is more pronounced due to its larger flux and perhaps other unknown factors such as alignment of the tube in its holder. All the other tubes show essentially no dependence of rejection on velocity. One surprising result is that of the dependence of flux on velocity which is pronounced on tube #16 but also apparent on the other tubes. No mechanism is proposed to explain this observed behavior.

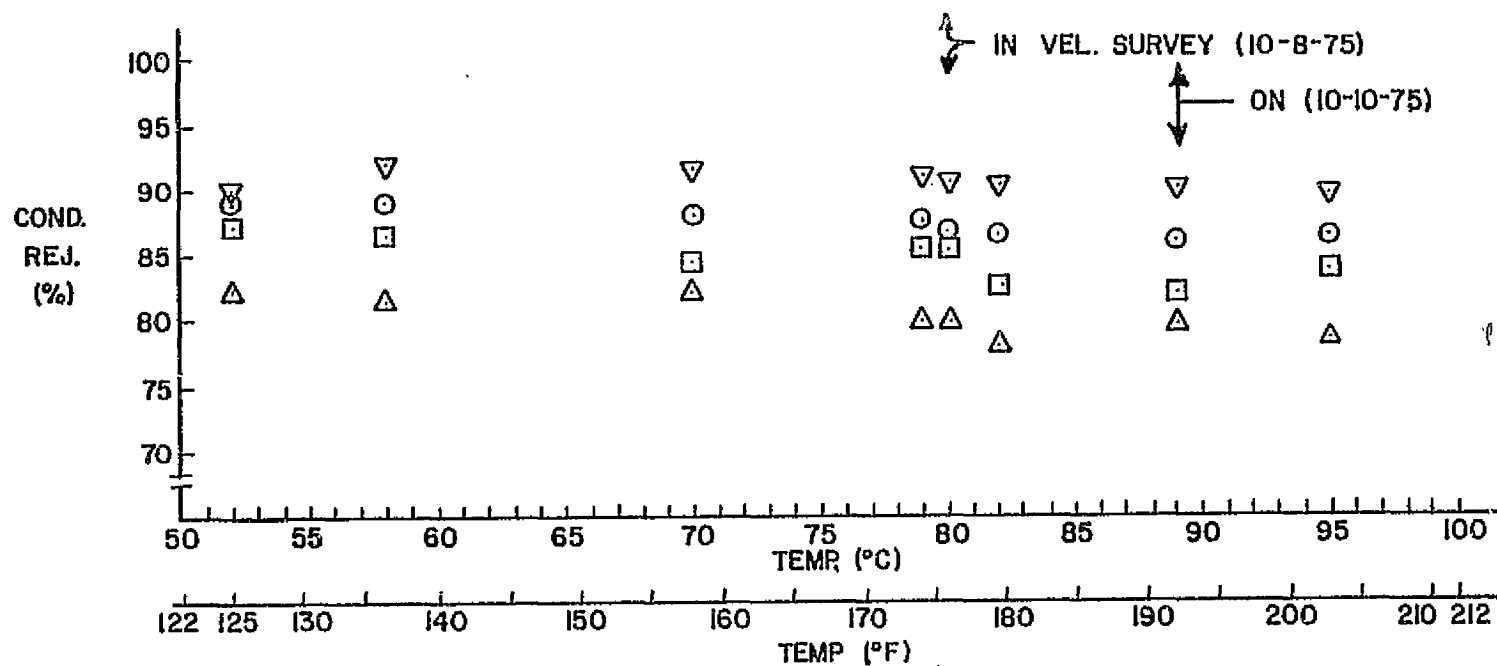
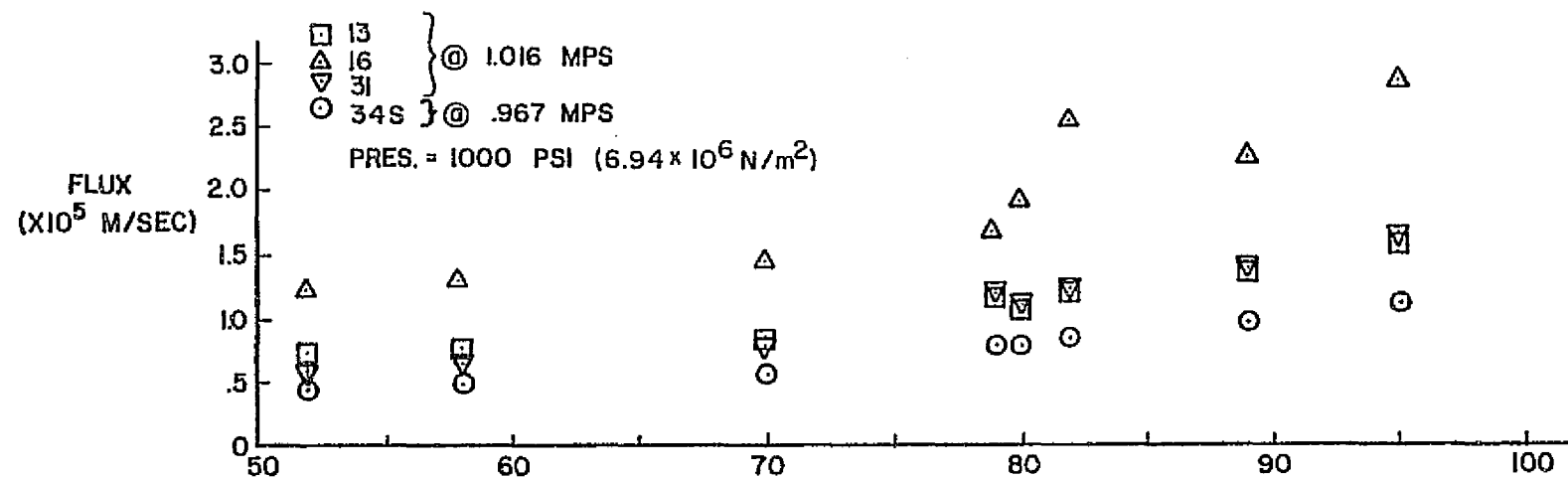


Figure 12. Parametric effect of temperature.

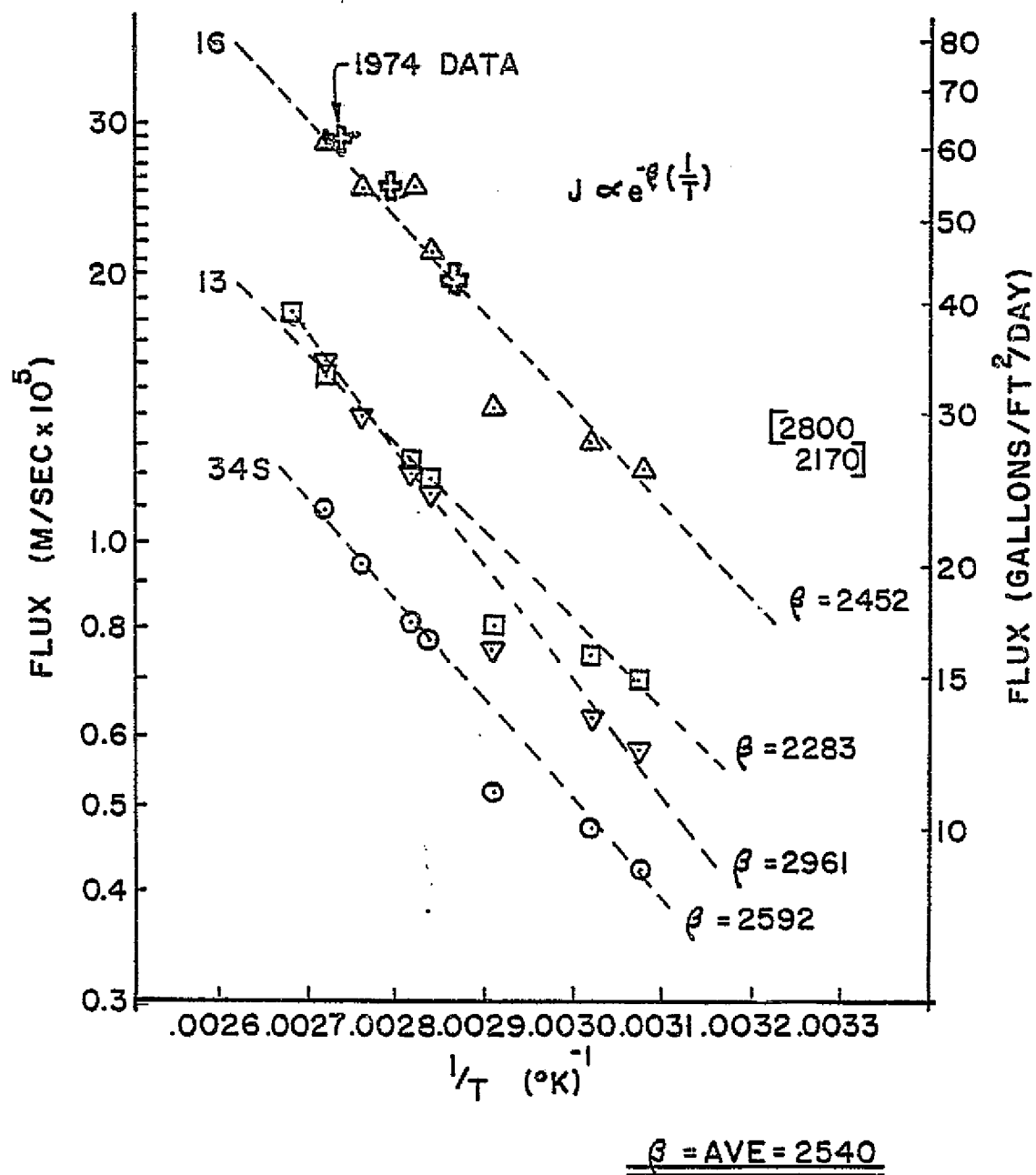


FIGURE 13 CORRELATION OF FLUX WITH RECIPROCAL TEMPERATURE

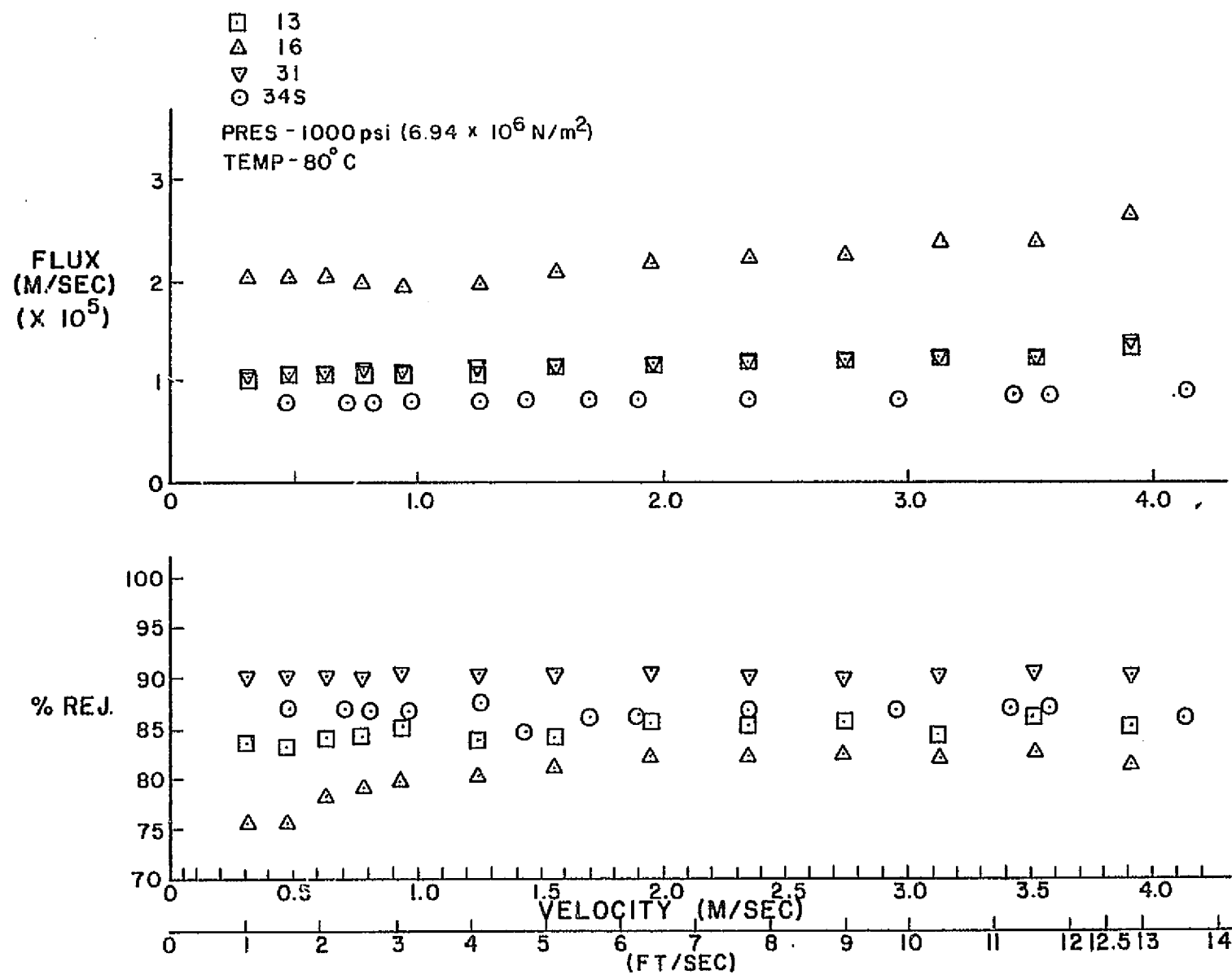


Figure 14. Parametric effect of velocity.

At the conclusion of the ninety-day test, some additional testing was performed. Concentrations of detergent up to 6000 mg/l were administered in an increasing amount to a solution containing 100 mg/l of salt solution. No increase in flux nor decrease in rejection (conductivity) was noted. In fact, a substantial rejection increase was noted. Serial amounts of cationic detergent Cetol produced considerable turbidity in the feed stream but had no substantial effect otherwise. These results, compared to Reference 10 data, simply imply the ZOPA membrane to be unaffected by anionic detergent as was the PSAL membrane of Reference 10.

Because of the prospect of urea pretreatment by NaOCl, the membranes were subjected to 300 mg/l NaOCl. Within fifteen minutes the flux of the steel membrane was enormous (gushing) and the loop was shut down. After removal of the steel membrane, the ceramic membranes also quickly failed.

Photographs of the membranes immediately after removal are shown in Figures 15 through 18. Examination of the membrane surface of the steel support was not possible due to its inside-out flow. All ceramic tubes had blackened surfaces covered by a thin layer of residue. Tube #31 was broken during extraction. No evidence of any tendency to plugging was found; the presence of lint was not evident. It is considered that the 20-micron prefilter used was adequate for use with the tubular membranes.

For reference, a set of data have been selected as representative points indicating the product water quality. Table 5 displays these data. Included are values of ammonia, urea, conductivity, total organic carbon, odor, and foaming. The results for urea and ammonia are not representative of on-line operation because of their reactivity and volatility. The values of conductivity and TOC are expected to be representative. The average product water should be approximately the numerical average of the data shown. It is difficult to predict the mixed properties of odor and foaming. Bench tests of foaming indicate that trace foaming occurs at 1 mg/l of the detergent used, so that the complete elimination of foaming will require near perfect rejection. Consider the data at hour 305 of Table 5 for TOC and foaming. Tube #13 shows foaming of 0.5 inches with the second lowest TOC reading; tube #31 shows a tract of foaming with the highest TOC reading. Thus no exact correlation of TOC and foaming is apparent. It is suspected that the several candidate cleansing agents will show different tendencies to foaming and that the foaming data will only be meaningful with a fully mixed product. Despite these reservations, the data suggest that the attainment of zero foaming will not be expected by membrane filtration alone.

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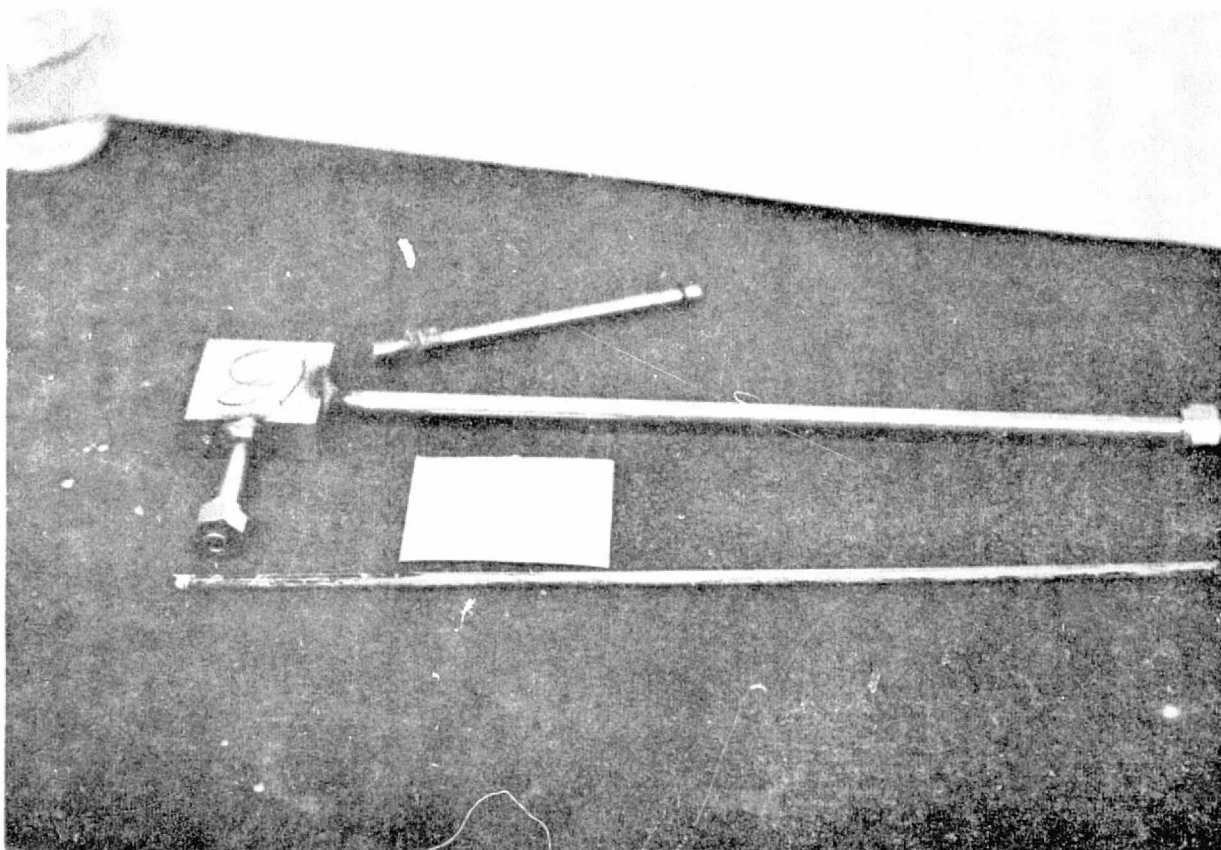


Figure 15. Photograph of Tube 13 after Testing

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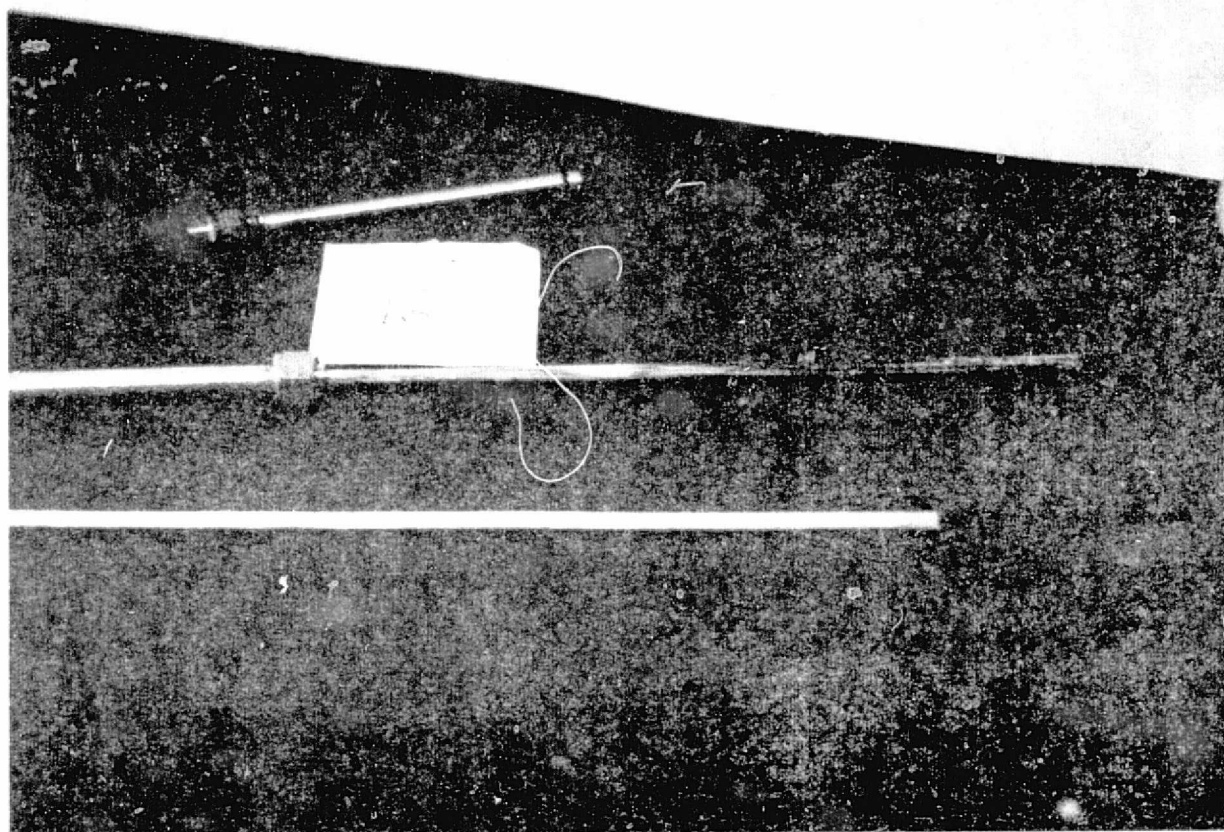


Figure 16. Photograph of Tube 16 after Testing

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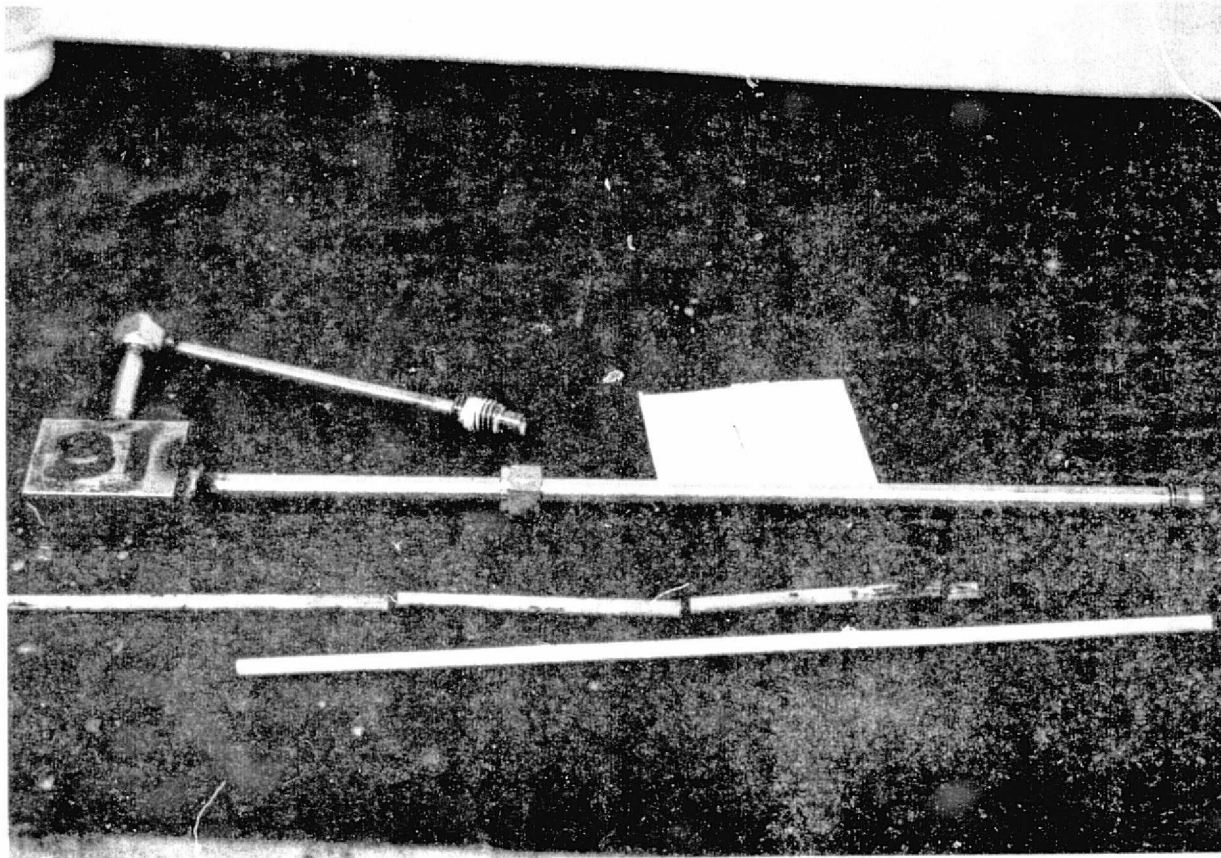


Figure 17. Photograph of Tube 31 after Testing

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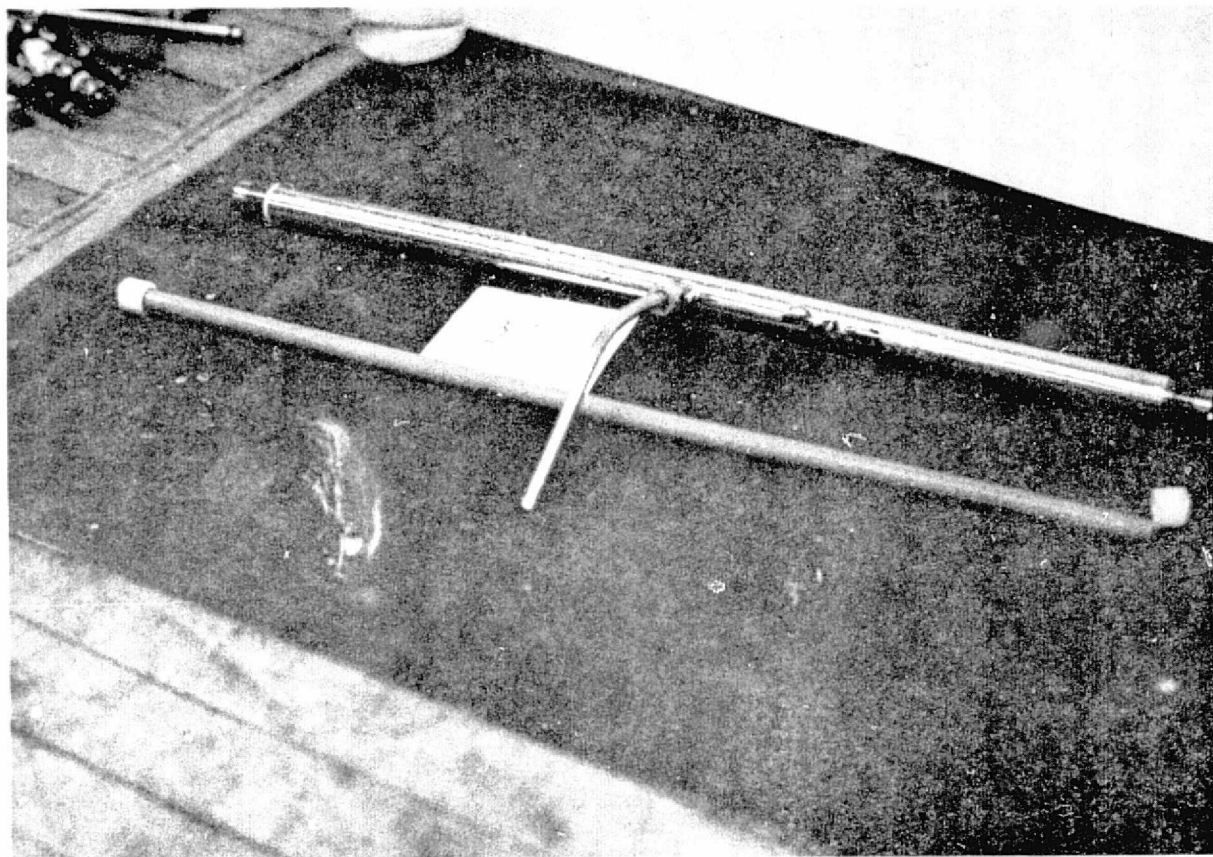


Figure 18. Photograph of Tube 34S after Testing

TABLE 5. SELECTED PRODUCT WATER QUALITY RESULTS

ELAPSE TIME	TUBE 13				TUBE 16				TUBE 31				TUBE 34S					
	NH ₃ (ppm)	UREA (ppm)	COND (µmho)	TOC (ppm)	O (1)	F (2)	NH ₃ (ppm)	UREA (ppm)	COND (µmho)	TOC (ppm)	O (1)	F (2)	NH ₃ (ppm)	UREA (ppm)	COND (µmho)	TOC (ppm)	O (1)	F (2)
0	.15	14.0	15.5	19	N	S	.21	14.6	15.5	17	N	S	.30	15.2	20.0	19	N	S
51	2.24	6.45	19.0				1.76	8.63	19.5				3.42	10.4	17.5			
95	3.61	7.49	26.0				3.04	8.61	24.0		S	S	3.61	9.56	21.5		N	T
140	3.79	7.86	33.0	23	S	S	3.61	8.01	35.0	26	N	T	4.38	6.18	27.5	18	N	T
165	2.11	8.99	33.5	21	N	T	3.27	9.96	38.0	25	S	S	2.44	10.4	25.0	20	N	T
215	6.17	18.1	47.0		S	S	5.60	17.5	53.0		S	S	4.18	13.9	34.0		N	T
262	7.50	13.4	85.5		S	.01	10.1	8.02	90.5		S	.125	3.98	10.9	40.0		N	T
305	11.6	16.4	105	89	ST	.50	9.12	16.3	220	88	S	.25	8.69	11.2	85.0	96	N	T
325	10.6	14.9	155		ST	.25	12.8	7.09	175		ST	.25	11.6	9.29	70		N	T
368	11.6	2.51	175		S	.50	10.6	5.05	205		S	.50	9.12	5.04	74.5		S	N
419	9.89	2.76	260		ST	.5	10.9	7.84	270		S	.5	5.76	6.29	100		N	T
485	8.53	2.93	310		S	.5	8.53	2.93	360		S	.5	4.26	2.39	130		N	T
536	7.36	6.60	42	20	N	S	5.76	5.71	49	3	S	S	5.43	6.56	41	11	N	T
609	8.53	2.93	53.5		S	S	11.5	7.29	53.5		S	S	9.42	2.05	36		N	T
683	7.36	2.05	51		S	.125	6.51	3.88	59		S	.125	4.97	6.50	31		N	T
750	7.73	1.68	55.5		S	.125	7.01	2.88	64		S	.125	4.97	3.57	29.5		N	T
797	2.12	4.20	62.5	30	S	S	3.05	5.59	73.5	36	S	S	1.55	4.15	34.5	8	N	T
849	4.87	6.94	72		S	S	5.70	6.12	89		N	T	3.21	4.99	38.0		N	T
942	3.05	1.34	92		S	.01	4.39	0.23	140		S	.125	2.47	0.74	50		N	T
1038	4.17	2.49	140		S	.1	6.00	2.20	180		S	.1	2.61	1.56	50		N	T
1105			175	72					235	96					68	18		
1152	6.00	1.79	105		S	.01	6.00	1.39	145		ST	.01	3.96	3.44	58		N	T
1226	6.66	*5.79	115		S	.12	6.66	*2.44	145		S	.12	4.17	*2.49	47.5		N	T
1274	5.70	*3.12	130		S	.01	6.66	*7.89	195		S	.25	3.39	*6.21	58		N	T
1351	11.82	0	210		S	S	10.11	3.01	285		S	.12	5.41	2.80	79		N	T
1415	10.3	7.19	230		S	S	11.5	11.3	310		S	.5	3.80	8.98	86.5		N	T
1468	20.5	18.2	440		S	.25	33.0	20.1	600		S	1.0	9.31	16.1	160		N	T
1482	12.1	8.42	120		S	S	10.9	8.58	140		S	.12	5.79	7.68	55		N	T
1545	16.6	5.02	145		S	S	12.1	13.3	170		S	.12	8.83	6.95	56.5		N	T
1609	10.9	3.29	140		S	.01	10.9	4.06	195		S	.25	4.69	5.12	54		N	T
1729	7.36	4.01	205		S	S	10.5	3.42	295		S	.50	5.14	2.60	74		N	T
1776	11.7	-0.	275		S	.01	11.7	.61	425		S	.50	4.41	1.00	100		N	T
1824	6.00	5.67	390		S	.01	13.6	7.95	575		S	.25	3.60	3.40	150		N	T
1879	4.89	5.12	185		S	T	5.41	1.58	245		S	.10	2.65	2.50	70		N	T
1945	16.0	-0.	340		S	.12	18.9	-0.	435		S	.50	10.8	1.27	130		S	T
1994	16.0	22.9	615		S	.25	21.1	20.0	730		ST	.75	8.21	8.69	200		S	T
2090	3.37	5.17	40		S	.01	1.85	8.78	49		S	.25	2.30	4.95	20		N	T

(1) Odor: N-None, S-Slight, M-Mild, ST-Strong

*Urea Additions (0.5gm)

(2) Foaming (15 sec.): N-None, T-Trace, S-Slight, Meas inches

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3.2.4 Conclusions

- (1) Of four membranes subjected to the ninety-day test, all completed the testing.
- (2) Flux declines occurred over the entire period, subject to flux increases associated with lower feed concentrations. These declines must be considered in the design of the system control scheme.
- (3) No significant losses in membrane solute rejection were associated with the extended operation.
- (4) A membrane on stainless steel ranked high in both flux stability and solute rejection.
- (5) One-pass filtration is expected to suffice for meeting all water requirements except ammonia and foaming. Multi-pass filtration will improve these qualities, but the reduction in urea concentration to preclude ammonia production may be impractical.

3.3 OPTIMIZATION ANALYSIS

An analysis to determine the "optimum" membrane was contrived. The analysis sought to minimize a total weight penalty which was composed of (1) the weight of the module (dry), (2) the weight of pump and motor, (3) the weight penalty associated with power used to drive the motor, (4) the weight penalty associated with heating the water to operating temperature, and (5) the weight of water not recovered to a level such that the concentrate exceeds 25 lb/day, which is the allowed influx to the vapor compression/distillation unit.

The analysis presumed the system configured as in Figure 19. Water from the shower and clothes wash is heated to process temperature over a designated period. It then is processed with the purified permeate being recirculated to the feed until the improving quality allows it to meet a standard. As soon as the standard is met, the permeate is allowed to replenish the shower water supply. All during operation, a constant flow rate of concentrate is allowed to pass to the feed of the vapor compression/distillation unit.

The parameters considered in the analysis were (1) the lowest flow rate of fluid in the last single-tube element, (2) the velocity above which a prospective branch to more tubes (viewed from downstream) would occur, (3) the module recovery, (4) the operating outlet pressure, and (5) the operating temperature. Starting from the outlet end of the module, the current lowest flow rate is assigned at the operating pressure and temperature. The last tube element permeate flow and rejection characteristics are calculated to yield the

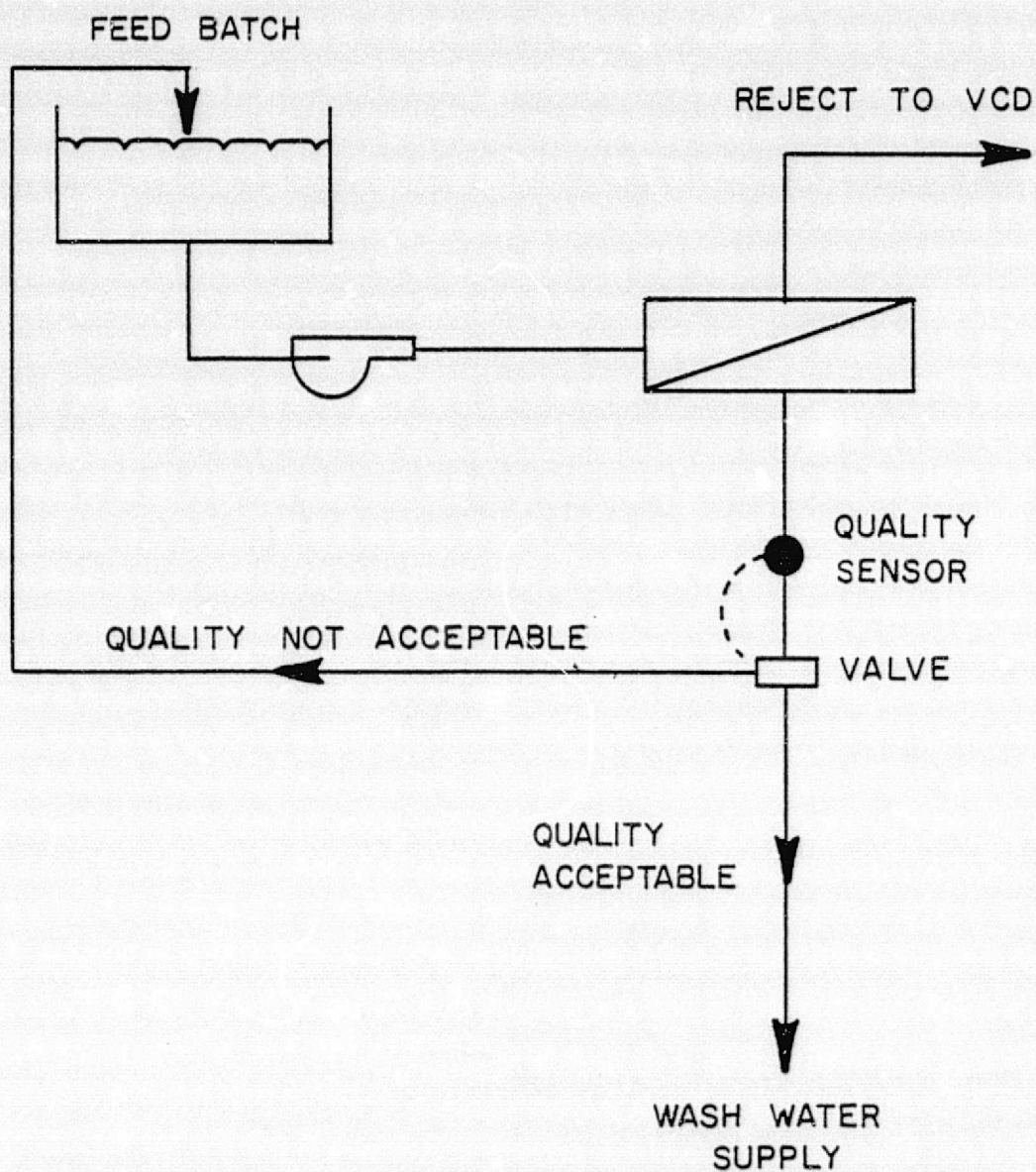


Figure 19. System schematic used to calculate optimum system.

conditions at the entry of the last tube element. A test is made to determine whether the current recovery estimate has been achieved. If it has, the module design is complete. If not, a calculation of the velocity which would occur in one plus the current number of tubes is made. If this velocity is high enough the flow is divided into one greater than the current number of tubes and the calculation proceeds upstream.

As soon as the module is thus designed, its overall rejection of the following items is known: sodium chloride, potassium chloride, urea, total organics, conductivity, and ammonia. The feed levels of each of these is input and the module operates on the feed until each of the six items achieves its specified level of presence in the permeate. The weight penalty is then calculated.

The foregoing constitutes a single calculation. Each parameter is allowed to vary to greater and lesser values and the corresponding weight variation used to allow new parameters to be considered which are, at each step, improvements in the weight penalty. This "hill climber" technique is used until no improvement can be made.

The internal calculations for rejection and flux dependence were based on models in agreement with the parametric test data. Specifically, an exponential rise with pressure to an asymptotic rejection was fit to the observed data, and the asymptotic rejection was independent of temperature. The flux was considered proportional to pressure and to $\exp(-2540/T)$ in agreement with observation. Data from testing agrees reasonably with theoretical models for diffusion rates [11] and these theoretical models have been used for the calculation of the concentration polarization effect. We have used data for salt for the diffusion coefficient of salt, urea, and ammonia and almost arbitrarily used one-half that value for the diffusion of "total organic" material. All diffusion rates are adjusted for temperature in proportion to temperature and inversely with viscosity.

Values of power penalty of 0.44 kg/watt were employed. The pump and motor weight was deemed proportional to power with a proportionality factor derived from Reference 12 to be 0.121 kg/watt. The water heat was assumed to be produced at 0.44 kg/watt penalty and the inflow was heated continuously to reduce the penalty as much as possible. A lower penalty heat source could provide the same energy and be applied to heat the water faster. At the 100 kg/day influx the weight penalty for heating to 347°K from 305°K was 89 kg (i.e., 203 watt). The module physical weight was estimated as the weight of tubes plus the weight of the headers. The header diameter is estimated based on the number of tubes allowing approximately 1 mm tube spacing and 10% excess over the minimum diameter to incapsulate the tubes. The header mass was estimated to be 175 kg for one meter in diameter and scales with the diameter squared.

Calculations were performed using the above model and the feed and product requirements in the table below, which also shows the achieved quality.

	<u>Feed</u>	<u>Required Product</u>	<u>Membrane Rejection</u>	<u>Achieved Product</u>
NaCl	50	450	0.92	5.0
KCl	10	100	0.90	1.4
NH ₃	24	5	0.89	3.8
TOC	750	50	0.96	50.0
Urea	50	50	0.70	25.0

The calculations were also performed using different values of input membrane rejections, chiefly for ammonia. At lower ammonia rejections, the TOC index no longer is the limiting factor.

Other observations were made. Despite the substantial penalty for heating the water, high temperatures definitely calculated to be beneficial primarily because of the decrease in diffusion resistance thus aiding rejection. Optimum temperatures were 75°C to 85°C depending on other factors. The incentive to achieve high water recovery showed itself as if a constraint, always achieving within the smallest division the "goal" recovery. We assume this means that higher recovery could be achieved with relatively small penalty, though no calculation was attempted.

In serial inputs of different flux values, we found a preference for fluxes of 1×10^{-5} m/sec. This flux was adopted as the design value thus providing the flux value preferred by calculation. The reason for the preference is in the concentration-polarization derived penalty versus the actual weight of the module.

3.4 UREA/AMMONIA CONTROL

The above optimization calculation has been used as a guide for problem solving. It is clear that the technical problem is in separation nitrogen convertible to NH₃ and TOC. Though the present formal water specification allows 50 mg/% of urea, such urea is reactive in the product water to produce NH₃. Thus the NH₃ problem becomes worsened. Previous investigators [13, 14] have considered conversion of urea to ammonia before processing. This procedure increases the assumed load by more than 100% for NH₃; such increase cannot be readily handled. The investigators proposing this scheme have based their proposition on rejections of NH₃ as NH₄⁺ in slightly acid solutions. However, in slightly alkaline solutions some fraction of ammonia will exist as NH₃ in solution and will substantially reduce the rejection. Since the feed is complicated and highly variable, it was felt that some special treatment for urea or urea/ammonia be considered. With

reasonable control the separation of heavy organics becomes the membrane's chief requirement, which it performs well.

Two approaches were considered: (1) the identification of large (~500 mw) molecules which would selectively combine with urea to inhibit its breakdown into NH_3 at elevated temperature and to enhance its rejection, and (2) the identification of materials to cause the decomposition of urea into nitrogen gas and carbon dioxide in water and which might also hydrolyze the ammonia.

A chemical, xanthidrol, offered the possibility of complexing with urea with minimal prospects for medical effects. Bench tests were conducted with xanthidrol added to 50 mg/l solutions of urea at room temperature and at elevated temperature. The urea content was measured by exposure to urease converting urea to NH_4^+ , raising the pH to cause $\text{NH}_4^+ \rightarrow \text{NH}_3$, and the use of a specific-ion probe. In repeated attempts, no reduction in urea was achieved. Trials were made at low pH as favored by the complexing reaction chemistry. Phosphoric acid was used to reduce the pH and in this case the xanthidrol did effect a substantial reduction in urea below pH of about 4. No other molecule was found which appeared to offer urea complexing capability in neutral solutions.

Several chemicals were proposed which could cause the hydrolysis of urea to N_2 and CO_2 . Iodine, hypochlorite, nitrite, and perchlorate were suggested. The latter two were discounted because of explosive hazard and medical considerations. Iodine (in Lugol's solution) was evaluated in a bench test to allow up to 25% reduction in the urea content. Hypochlorite (in ordinary 5% bleach solution) allowed essentially complete extinction of urea. Also, according to Reference 15, the chlorine in hypochlorite solution is effective in reducing ammonia as well.

The hypochlorite approach offers several advantages. First, it is effective. Second, it has a widespread, well-known, and safe record allowing a high probability of medical acceptance. Certain chloramines may be produced with some undesirable effects. This problem is somewhat speculative, i.e., see Reference 15. To administer the correct dose of chemicals presents a small problem which may result in an excess of hypochlorite. Tests with 300 mg/l hypochlorite quickly failed the membrane. Additional tests at 5 mg/l were run for eight hours with no effect, though the material may have been driven from the solution thus diminishing its exposure.

We ran tests with powdered (ground) cobaltous hydroxide and fine-powdered cobalt metal to determine the catalytic effect on OCl^- decomposition. The materials were captured on two 20-micron filter elements and test solutions were passed through the filters at a rate of about 200 ml/min (which is the membrane production rate). The flow rate was varied in serial testing, to determine the flow rate at

which 90% extinction was registered. Table 6 shows the results in terms of powder added, liters of solution processed, and the flow rate at 90% extinction. With 20 g of -400 mesh cobalt, no more than a slight time effect is noted. Apparently the time of contact is favorable to the use of either material to decompose the hypochlorite.

The data in Table 6 suggest that small amounts of the finely divided material is sufficient, that flow rates of 200 ml/min (0.05 GPM) may be 90% purged of hypochlorite, and that the life or throughput capacity has not been reached in the experiments. The action described is accompanied by a slight decrease in pH, from about 8.0 to 7.2 on the average. Our laboratory water is normally slightly acid (pH = 6.2). The presence of OCl^- probably contributes to the formation of OH^- which is diminished upon the hypochlorite extinction. In the shower water system more complicated reactions are expected.

We conclude that hypochlorite can be used to control urea/ammonia nitrogen. Whether it should be administered to the feed or permeate is a system study subject. Administered to the feed, no urea or ammonia would be passed on to the VCD device avoiding possible odor difficulties there. Any gas production would tend to be limited to the feed tank rather than in feed and product reservoirs. The effect of any by-products of reaction would be mitigated by passage through the membrane. On the other hand, hypochlorite administered to the permeate would be consumed in a lower amount for a weight savings.

3.5 BREADBOARD TEST ITEM DESIGN

Modules of either ceramic or stainless steel tubes were considered for conceptual design. Because of the obvious susceptibility of the ceramic tube to fracture in an extreme mechanical environment, the steel tube was selected. However, there are other considerations which are pertinent to the design. The ceramic tube must be used in outside pressurization so that a pressure shell must be provided and each tube must have a flow channel surrounding it. The pressure shell and flow channel could be the same part or be separate. This arrangement provides an active perimeter of 1.67 cm within a capsule of 0.78 cm diameter. The steel tube provides 0.21 cm of perimeter within a diameter of 0.635 cm. Thus the ceramic membrane surface density is superior. Various schemes have been attempted for joining ceramic to metal with limited success. We used mostly simple O-rings for our laboratory seals, but attempted shear joints using commercial epoxy. These shear joints had clearances of approximately 0.1 mm which could be too small to distribute the thermal expansion strain without failure. However, we experienced few successful joints. Other fabricators produce more reliable joints but considerable dimensional instability and warping seems to characterize the

Table 6. HYPOCHLORITE EXTINCTION RESULTS

CO(OH) ₂		
<u>Amount Powder</u>	100 mg/l Solution	<u>Flow Rate in ml/min at 90% Extinction</u>
	<u>Accumulated Throughflow (liters)</u>	
50 grams	0 → 30	90
Add 50 grams	0 → 30	120
	30 → 60	300

Cobalt		
<u>Amount Powder</u>	100 mg/l Solution	<u>Flow Rate in ml/min at 90% Extinction</u>
	<u>Accumulated Throughflow (liters)</u>	
10 grams	0	200
	25	100
Add 10 grams	20	250
	40	800
	66	300
	96	75
	112	120
	132	220
After six weeks	152	200

assembly. One suggestion not attempted by us was to metallize the ceramic and braze it into place. Such a joint may also experience thermal expansion problems. In conclusion no really satisfactory joint was developed. Joining the stainless steel tubes is considerably easier though there still is a potential problem during thermal transients due to expansion if an all-brazed assembly is used.

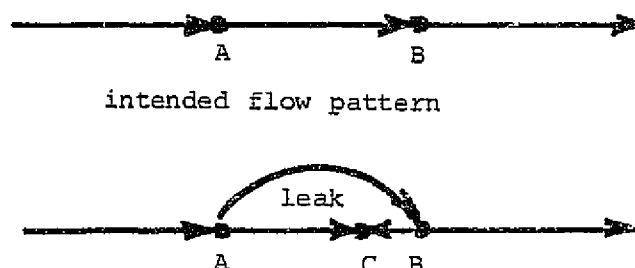
Discussions were conducted with the manufacturer of stainless steel tubes concerning available sizes. Sizes of 0.31 cm inside diameter were initially procured and a step made to 0.17 cm inside diameter finally. It was important to employ as small of a diameter as reasonable to encourage higher velocity with the small quantity of fluid flow. Limitations of the manufacturing process did not allow reduction of the tube outside diameter or increase of length, which remained at 0.62 cm and 30.5 cm, respectively. The tubes were fitted with end caps incorporating O-rings. The manufacturer welds and anneals the part with substantial reliability.

The design was based on the use of tubes having inside diameters of $0.17 \text{ cm} \pm 0.02 \text{ cm}$ and on fluxes from the ninety-day test experience. These fluxes averaged $0.6 \times 10^{-5} \text{ m/sec}$ near the end of testing for the stainless steel test article with short-term drops to near $0.4 \times 10^{-5} \text{ m/sec}$. Based on a daily input of 100 kg of shower water, or 0.1 m^3 , the area required to achieve 90% recovery was estimated. It was assumed that the processing would require twelve hours, or 43,200 seconds, so the average flow rate of permeate is $0.09 \text{ m}^3/43,200 \text{ sec}$ or $2.1 \times 10^{-6} \text{ m/sec}$. The membrane area is this value divided into the flux $0.6 \times 10^{-5} \text{ m/sec}$, or area = 0.288 m^2 . Each tube has an area of $16 \times 10^{-4} \text{ m}^2$, so approximately 180 tubes are needed. In more detailed calculations of performance a design of 192 tubes was finalized. Simple system comparisons with a single tube in series or two parallel tubes followed by a single tube proved only slightly different since the single tube design predicts only about 100 psi ($6.9 \times 10^5 \text{ N/m}^2$) overall pressure drop.

Other considerations for module design were concerned with making provision for membrane formation. During membrane formation it is generally necessary to achieve a minimum pressure and velocity for acceptable performance. The velocity requirement may be poorly founded; historical specifications of 10 m/sec contrast with good formations observed at 0.3 m/sec. With flux values of 10^{-4} m/sec in a single tube of area 0.307 m^2 the permeate outflow is $3 \times 10^{-5} \text{ m}^3/\text{sec}$ causing an inflow velocity 13 m/sec greater than the exit tube velocity. This leads to high pressure drops and hence low pressures at the exit of the module. We chose to form membranes in five to eight parallel channels to reduce this tendency. The alternative is to form tubes individually, which is a lengthy process.

The design conceived to allow for all these factors is shown in

Figure 20. The individual tubes are sealed by O-rings into the tubesheets appropriately spaced. On each of these tubesheets is mounted a plate having channels allowing flow to cross over between selected pairs of tubes. These flow-routing plates may be removed without disturbing the seal on the tubes. Sealing between tubes is accomplished by a flat seal material. The high-pressure seal around the tubesheet and flow-routing plate is by O-ring. The tie rods are sealed by compression of a flat washer thus preventing flow directly to the product chamber. Three seal failure modes may be identified: flow of concentrate to product, interchannel concentrate flow, and flow to outside of module. The latter does not affect the rejection performance while the former two do. The interchannel flow of concentrate affects the performance as indicated by the following schematic diagram.



The intended flow pattern is as shown in the upper portion while a leak from point A to point B, if of sufficient magnitude, causes reverse flow from B toward point A. The velocities near the no-flow point C are small and all rejected material simply accumulates. In a growing region near C, the permeate produced will have poor quality due to the concentration buildup and will thus affect the average permeate quality.

The potential for leaks may depend on dimensional variations and on the strains dependent on pressure forces. The original design has been modified in an attempt to counter the variations due to strains. The various forces which act on the surfaces are shown in Figure 21. Crude calculations suggest that the bending of the plates causes bending of an order of magnitude less than the stretching of the hardware; therefore, the plates are considered to be rigid. Force F_B is the constraining force of the perimeter bolts, F_T that of the tie rods, F_p that of the applied pressure, and F_G that of the gasket material. The loading area of Plate 1 is 0.0188 m^2

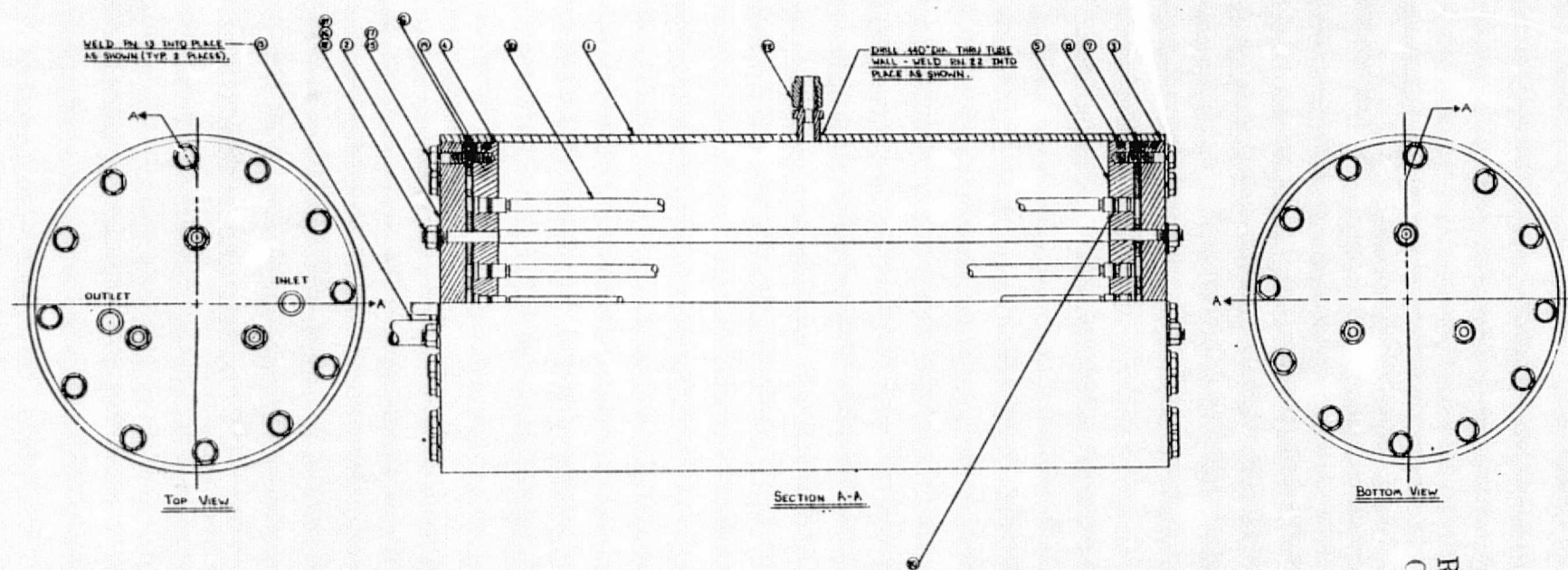


Figure 20. Hyperfiltration module breadboard unit.

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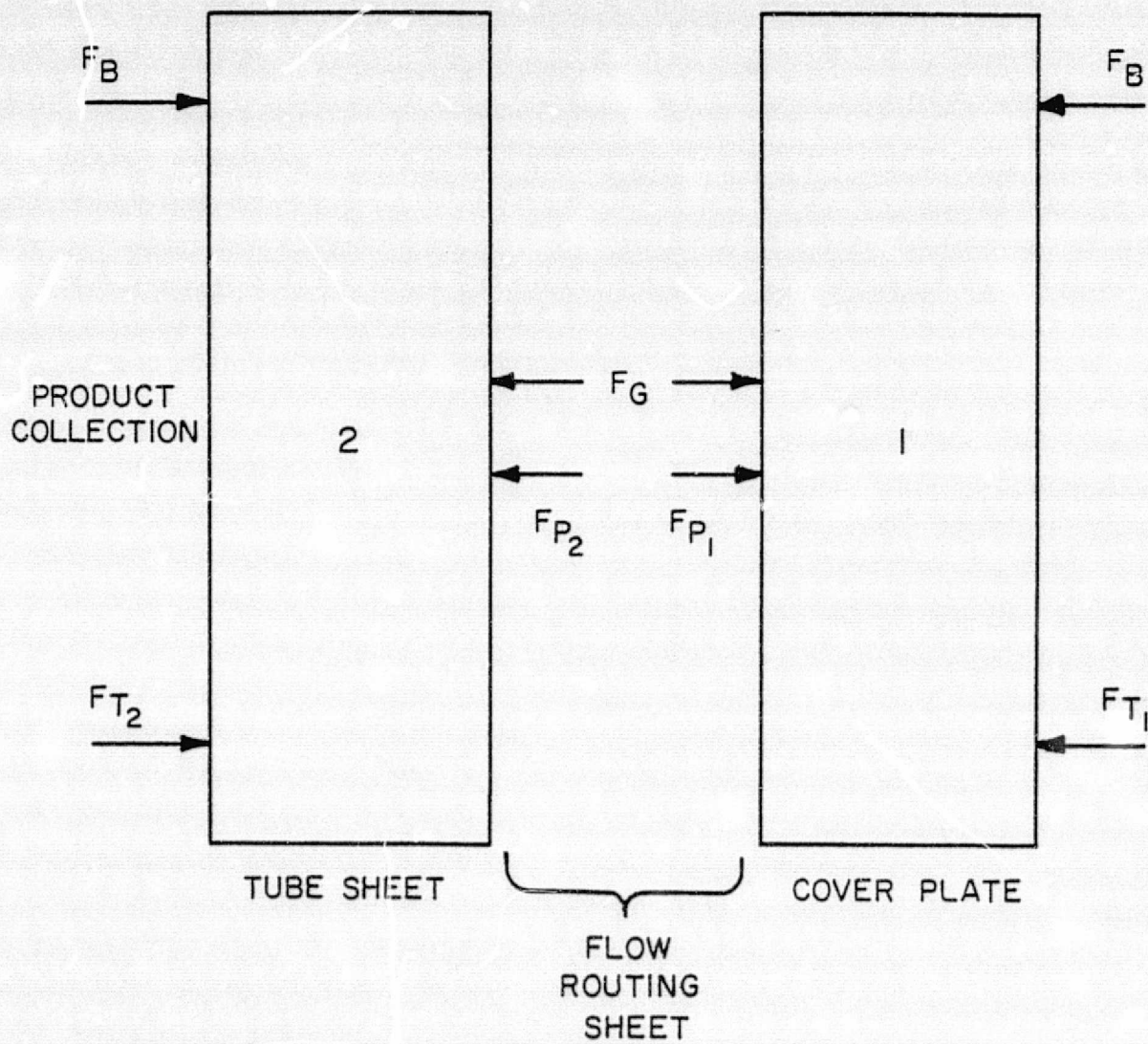


Figure 21. Schematic diagram of end details showing applied forces.

(29.2 in²), of Plate 2 is 0.0136 m² (21.14 in²). Whenever internal pressure is applied a net force of pressure $\times (A_1 - A_2)$ occurs to the right in Figure 20 which shows the force diagram for one end of the module. This force tends to reduce the force between the tie rod shoulder and Plate 2. In our early experience we torqued the fasteners to about 6.2 N-m (55 in-lb) or a compressive force of about 7.95 kN (1800 lb) per fastener depending on thread friction. Upon pressurization we failed one tie rod after some time, indicating a marginal problem. The other tie rods were stretched to the point that the nut would not advance readily in the stretched zone. Under this load, F_G was symmetric and amounted to about 120 kN (27,000 lb). F_{P1} was 129 kN (29,000 lb), and F_{P2} was 93 kN (21,000 lb) under full pressure. The load-deflection relation of the tie rods and bolts causes 1.5 units of load to be carried by each tie rod compared with 1 unit of load on each bolt. For twelve bolts and three tie rods, the force sharing is 27% on tie rods, 73% on bolts. All of the imbalance in force is carried in the tie rod. Thus, 213 kN (48,000 lb), ($F_G + F_{P2}$), was distributed to tie rods and bolts, and 36 kN (8000 lb), ($F_{P1} - F_{P2}$), was carried by only the tie rods. The forces amount to 31 kN (6990 lb) on each tie rod and 13 kN (2920 lb) on each bolt. Under this force the tie rods yielded. This simple analysis regards the gasket pressure as constant which it probably is not; some relief from these forces is expected.

After the first experience of tie rod breakage, the bolts were torqued to 1.7 - 2.3 N-m (15 - 20 in-lb) to yield a predicted preload of 2.7 kN (600 lb) each or $F_G = 40$ kN (9000 lb). Under this load pattern 35 kN is applied to the tie rods only while 129 kN is applied to the ensemble. These loads result in a 23.4 kN force on each tie bolt and a 7.85 kN force on each perimeter bolt. In this case also, the force between the tie rod shoulder and the tubesheet (F_{T2}) has been reduced to zero almost exactly. The stresses in the tie rod threads 627 MPa (91 kpsi) and on the bolts, 386 MPa (56 kpsi). Thus the tie rods are seen to be nearly stressed to limit and the bolts are heavily loaded. A third procedure of tightening only the perimeter bolts and just securing the tie bolts was also tried, but ultimately this procedure led to sufficient migration of the tubesheets that the O-rings on the tubes were extruded from their seats.

When it was discovered that the force on the tie rod shoulder could be reduced to zero, the flow-routing sheets were modified to accept positive O-ring seals. These seals were blamed for the leaks which actually were occurring at extruded O-rings on individual tubes, but the cause was finally discovered. Also, the enlargement of the area in the flow-routing sheet inevitably intersected some of the tube apertures so that interchannel cross flow could not be prevented. Therefore new flow-routing sheets were made which also improved the susceptibility to interchannel leakage by lowering the predicted

pressure differences and by forcing any involvement in interchannel flow to affect the minimum number of tubes.

The final design aid was a large external clamp which could be applied to reduce some of the load on the tie bolts and insure positive force on the tie rod shoulder. Also a technique of using silicone rubber as a gasket aid spread thinly on the gasket at application was considered positive. The tie rods were sealed to the tubesheets using Loctite products with variable success presumably due to the clearance and the passive nature of 300 series stainless steel.

The flow design and velocities are summarized in Table 7. The data presented are for the design condition wherein approximately twelve hours is required to process the daily flow. The pressure drop depends heavily on the exact diameter of the tubes but is predicted to be below 0.6 MPa.

3.6 BREADBOARD ITEM TESTING

The module was assembled with the 7-tube path header installed for membrane formation. Figure 22 shows the completed installation of the tubes and Figure 23 shows the module with the entrance plate installed. Even though adherence to the dimensional specifications for the O-rings was observed, considerable difficulty was experienced in installation. Lead-in chambers were added with a countersink which helped, but still there was conflict which led to some cutting of the rings. The cap screws and tie rod nuts were torqued evenly at 6.3 N-m (55 in-lb). The system was estimated to be uncontaminated following a formation on a sample tube with 80%, 1.5×10^{-5} m/sec (rejection, flux) performance. The module was washed in 1 molar HNO_3 and rinsed in RO permeate water. After addition of NaNO_3 and $\text{ZrO}(\text{NO}_3)_2$ to the system in double the usual concentration, no flux decline was registered in three hours. The system was again cleaned in 0.1 M HNO_3 and rinsed.

After the addition of 2 g $\text{ZrO}(\text{NO}_3)_2$ and five hours, a like amount of $\text{ZrO}(\text{NO}_3)_2$ was added. The permeability of the tubes had decreased until throughflow from entrance to exit could be achieved at six hours from start. After an overnight shutdown, the pumping was restored and the flux dropped to 2.5×10^{-4} m/sec and 10% rejection was achieved. The second step was initiated at this condition. The pH of the system was raised according to procedure even though the flux did not drop immediately upon addition of PAA. During the time from 0.5 hours to 1.7 hours from PAA addition the flux dropped to 3×10^{-5} m/sec observed at pH = 3.5. The formation pH schedule was followed until the membrane produced 71% rejection at 2.6×10^{-5} m/sec flux.

A regenerative step was conducted producing, after an overnight shutdown, 84% rejection at 1.3×10^{-5} m/sec flux. The membrane was operated for several hours and appeared to be stable. Upon installation

Table 7. DESIGN DIMENSIONS AND FLOW SUMMARY

Channel length (active)	60 mm
Active diameter	0.17 cm \pm 0.02
Inactive length (per tube)	1.55 cm
Inactive diameter	0.203 cm
Turn-arounds (rectangular)	0.254 x 0.475 cm
Inlet flow	3.77 kg/hr
Outlet flow (90% recovery)	0.37 kg/hr
Inlet velocity	1.01 m/sec
Outlet velocity	0.10 m/sec
Membrane area	0.3190 m ²
Membrane average flux	6.5 x 10 ⁻⁶ m/sec

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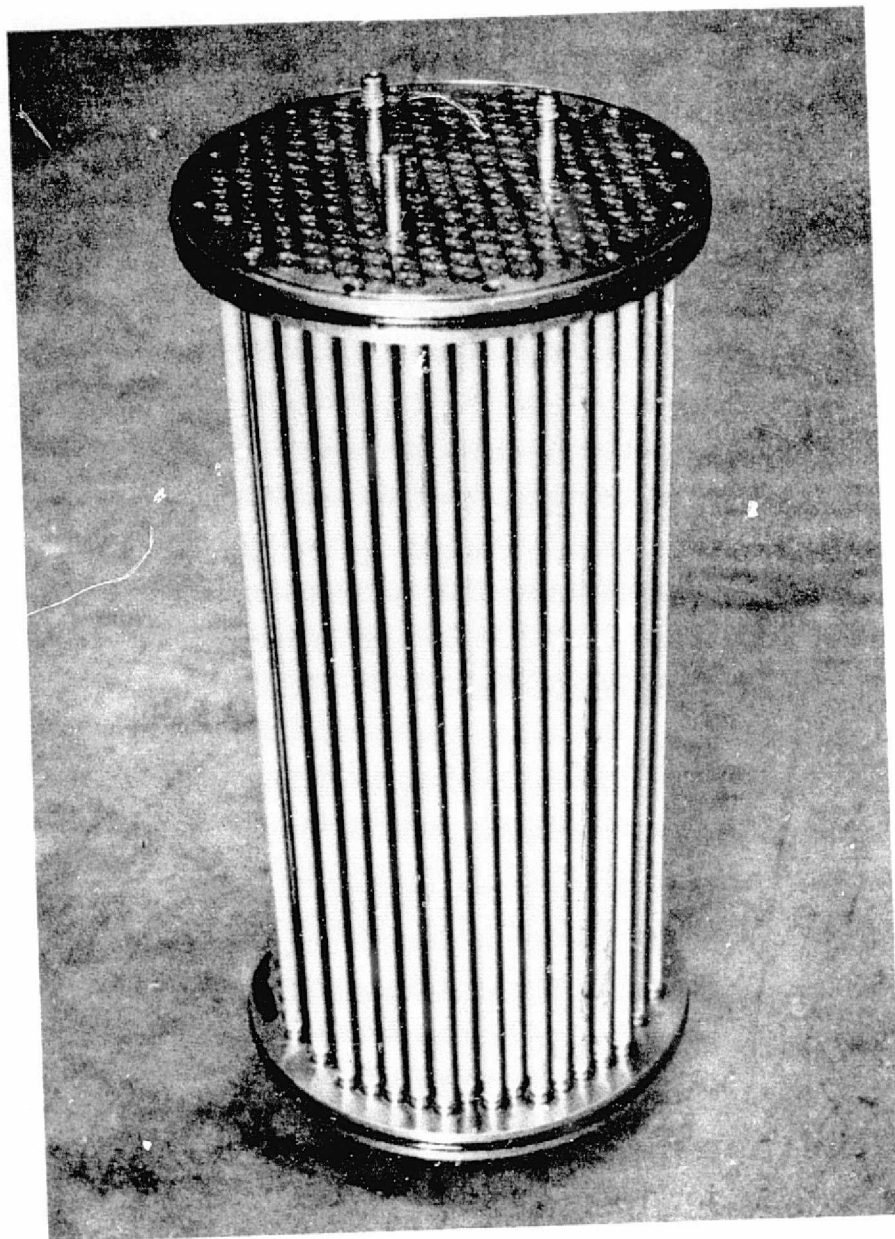


Figure 22. Photograph of breadboard unit
with tubes installed.

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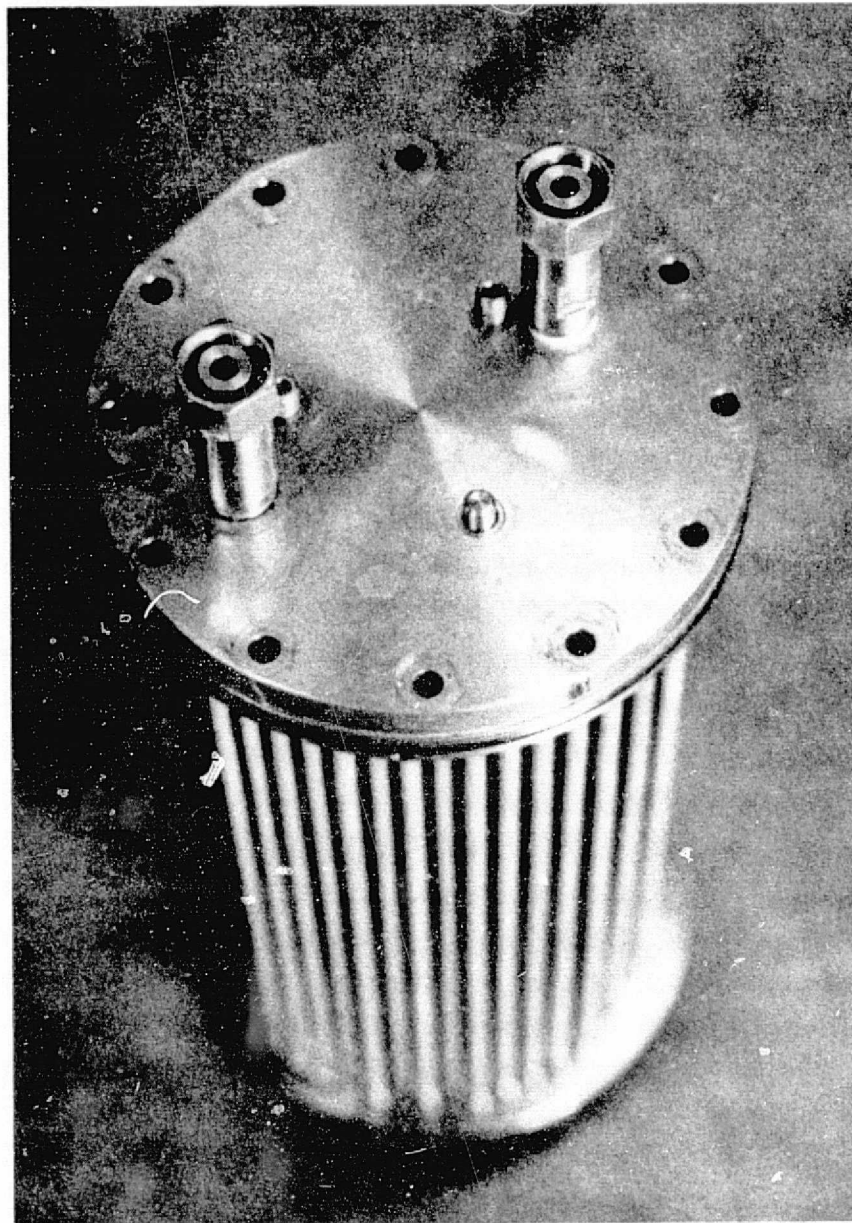


Figure 23. Photograph of module showing
inlet and outlet arrangement.

of the single pass header, the rejection dropped to 31% at essentially no flux change. The module was opened to inspect the flow path to insure proper assembly, which was confirmed. After reassembly a tie rod was broken. It was felt that hasty reassembly could have been responsible for uneven tightening of the tie rods, resulting in the fracture.

After fabrication of the new tie rod, the module was reassembled with new gaskets. Care was taken to tighten uniformly and release the residual torque from the tie rods and cap screws.

The rejection after reassembly achieved only 20% and some sudden increases in product flow rate occurred. Internal leaks were suspected. After verifying stable operation following a re-torquing exercise, a regeneration was attempted which did not increase the rejection. Another tie rod failure occurred.

We attempted to measure the bolt friction even though two stainless steel surfaces tend to gall producing large friction variations. Calculations showed the earlier torque produced a substantial fraction of the yield stress in the fasteners. We calculated a preload of 2670 N for the 5/16 inch fasteners and 1780 N for the 1/4 inch fasteners to correspond to 2.6 and 1.4 N-m torque, respectively. At this low level there is considerable uncertainty since the friction of the threads may amount to 1 or 2 N-m on some individuals. The torque levels actually produced over that for friction was estimated for all subsequent installations to be 1.5 N-m.

We measured the performance of individual tubes during the down period. Table 8 shows the performances noted in this evaluation. It was clear that the average rejection of 84% did not follow from these results. The tubes had been stored for several days partially (over half) immersed in water but the wicking effect only raises the liquid a few centimeters. In retrospect we consider that one end of the membrane had been allowed to dry out.

After reassembly of the module with the 7-tube header, its pressure drop character was measured. Figure 24 shows the pressure required to produce a given flow from the exit. The test was conducted at low pressure to prevent significant product flow effects. The data correspond to smooth tubes of diameter 1.5 mm quite closely. The membrane was stripped in NaOH until a flow of 1.5 l/min was produced. $\text{ZrO}(\text{NO}_3)_2$ was added in the normal amount with no change produced. The PAA step was executed and a rejection of 37% was observed. Large surges in flow suggested leaks which were observed at several of the small O-ring locations. The tie rod was again broken.

The careful analysis of forces reported in the design section

Table 8. INDIVIDUAL TUBE PERFORMANCE VALUES

<u>Flow (ml/min)</u>	<u>Rejection (%)</u>
12.30	15.0
8.60	18.0
1.20	50.0
1.00	61.0
1.10	37.0
0.80	54.0
3.07	51.0
2.53	23.0
1.12	45.0
1.28	40.0
1.16	42.0
1.40	40.0
1.50	34.0
1.30	13.0
0.26	79.0
1.00	89.0
1.90	14.0
3.00	11.0
1.20	84.0

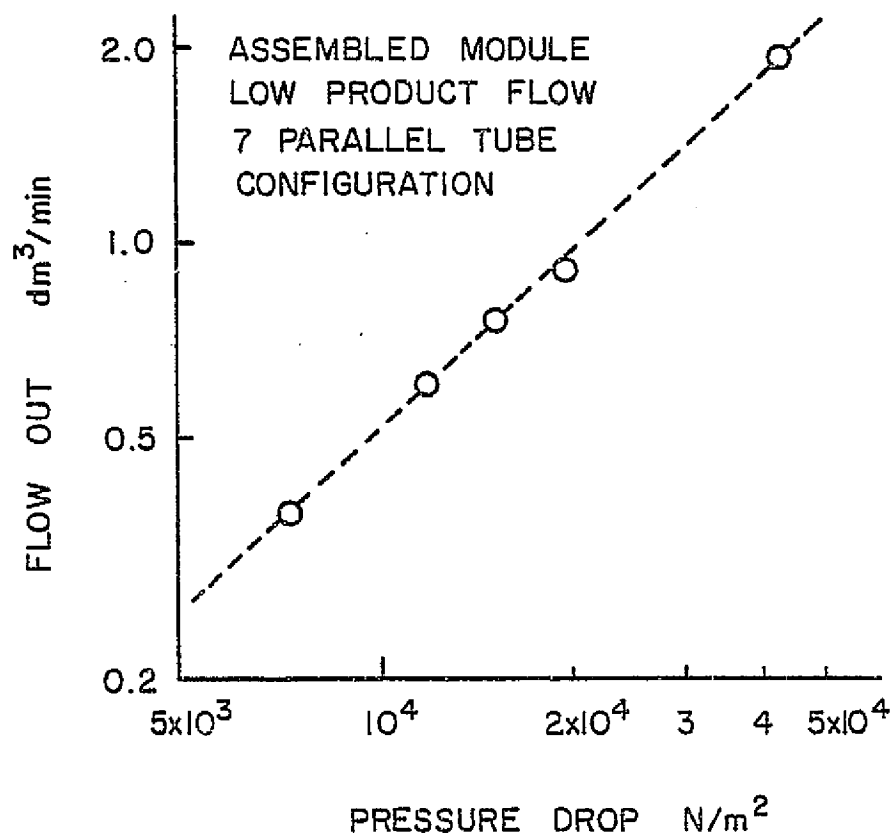


Figure 24. Pressure drop characteristics of assembled module.

was conducted. This analysis suggested that near maximum operating pressure, the tie rod shoulder could be unloaded and become a site for leakage. Indeed several rapid flow changes were observed. The tie rods were already overstressed so an alternative plan was followed. An enlargement in the hole around the tie rod could be formed to accommodate an O-ring for positive control of the flow through the tie rod penetration. Then the tie rod nuts could be loosely attached for best strength.

During the modification time we again tested individual tubes. Table 9 shows these results. The individual tubes were selected from both upstream and downstream locations, and represented each flow channel. There was no systematic non-uniformity noted by position. During the exercise, the membranes were allowed to dry out thus destroying their performance. Attempts to regenerate them were not successful.

The newly-modified header plates and new tie rod were assembled, the tubes cleaned, and a membrane reformed. A flow of 336 ml/min (1.8×10^{-5} m/sec flux) and 86% rejection was noted. Installation of the single-pass header brought poor rejection which a non-passing dye indicated to be not due to a leak. Careful examination of the flow paths clearly showed that the O-ring seal could not be accomplished without causing the flow path crossover.

We proceeded to redesign the headers since new ones would be required. Smaller widths of turn-arounds were used affording a greater gasket contact. Also, a new flow path was selected which would give even greater isolation of high- and low-pressure sections, especially near the tie rods.

The seal of the tie rod penetration was to be either by a Loctite compound or if required by silver solder. The former was judged better to avoid the possibility of complete stress transfer to the twelve peripheral bolts and would not risk warpage of the tube-sheet as would silver solder. We have had non-uniform success with the Loctite approach.

On the first trial, O-ring leaks by extrusion were discovered. The looseness of the tie rod nut allows enough motion of the tube-sheet to uncover the O-ring seal. During nut tightening to restore the tubesheet position, another tie rod was broken. A subsequent formation in single tube configuration showed 52% rejection but only 0.7×10^{-5} m/sec flux. Dye tests showed the existence of a leak around an O-ring. We concluded that an external clamp to aid the tie rods and new O-rings were required. These were procured. Also the tubes were cleaned and baked. A few trial formations on single tubes indicate the baking procedure will allow better flux in formation.

Table 9. INDIVIDUAL TUBE EVALUATION

<u>Flow</u> <u>(ml/min)</u>	<u>Rejection</u> <u>(%)</u>
0.40	86.0
0.50	85.0
0.60	88.7
0.87	86.0
0.40	83.0
0.50	88.0
0.30	86.0
0.50	88.0
0.30	87.0
0.30	80.0
0.30	89.0
0.40	91.0
0.35	91.0
0.37	90.0
0.40	91.0
0.10	90.0
0.54	88.0
0.33	83.0
0.19	82.0
0.30	84.0
0.46	84.0
0.303	84.0
0.26	81.0
0.29	74.0
0.22	79.0
0.19	78.0
0.16	80.0
0.29	70.0
0.62	76.0
0.46	86.0
0.32	84.0
0.138	90.0
0.12	91.0
0.35	74.0
0.38	81.0
-	89.0
-	76.0
0.84	87.0
0.78	88.0
<hr/>	
average of 35	0.36 ml/min. at 85%

Finally during refurbishment of the unit it was discovered that the tubesheet which allows O-ring seals with each individual tube was dished permanently and uniformly from edge to center. The magnitude of non-flatness is approximately 0.6 mm so that the flat seal cannot be reliable and further pursuit of module testing was discontinued. The mechanism of failure has been estimated as a simple overstressed condition of the tubesheet. The failure is readily predicted based on an analysis of the tubesheet under pressurization and without tie bolts as a constraint. Such a cylindrical plate simply supported at the edge with diameter 15.2 cm and thickness 1.27 cm, internally pressurized to 68 atmospheres, will deflect 0.038 cm at the center and have a maximum stress of 44% of ultimate strength. The exterior plates, having few holes, did not distort but the tubesheets having many holes did become offset.

The original design was conceived to provide the proper flow routing during operation and formation. The design was carefully fitted within an available shell size envelope. Stress and deflections calculations were made and the sizes of tension fasteners were increased to be stressed within design levels. Some of the stress models used had calculation errors of a slight effect and others, in retrospect, showed poor judgement. The failure was marginal judged from the fact that full pressure was applied for several hours before the first incident. Upon the first (or some) tie rod failure all models used for stress estimates were invalidated and the stresses in other parts became more than proportionately increased.

Deflections of the plate were calculated based on a 5 cm beam model loaded to design pressure levels. The calculation of deflection of the round plate with a hexagonal hole pattern was not attempted, under the premise that "zero deflection" resulted from the 5 cm beam and that the two-dimensional strengthening should produce even less deflection. Here, zero deflection means 0.0002 cm, or one-tenth of the bolt deflections. The stress levels were not calculated, under the guidance of experience relating small deflections to stress. Technical structuring of the 5 cm beam model also contributed possibly to problem underestimation, in that larger plate deflections than 0.0002 cm may be likely. At any rate, the 1.27 cm thick plate was forever decreed "rigid" and analysis of bolt deflections with the "rigid" plates was conducted. If, however, the beam had been modeled as 15 cm long (corresponding to absence of the tie rods) the deflections would have been estimated at about 0.016 cm or certainly not a rigid plate. When the plates began to distribute load to the tie rods, the tie rods yielded, allowing the plates to approach the maximum deflections corresponding to absent tie rods. At these deflections, the stresses in the hole-filled plate exceed the yield stress and permanent deflection resulted. The tie rod problems assumed to be due to torquing and loading problems really then appear to be related more to non-rigid plates and their transfer of pressure loading. The last effect is that the sealing surfaces are permanently deformed and must be redesigned.

3.7 IMPROVED TUBE PERFORMANCE

The pore structure of the stainless steel tube is different from the ceramic tube. The metal tube has more and larger pores. No estimate of the comparative fraction of surface area involved in pores has been made. The tube manufacturer uses the finest commercial grade powder (-325 mesh) for the 0.2 micron and 0.5 micron pore structure. He compresses the powder to a greater degree and modifies the sintering time to produce the 0.2 micron rating. Because of the difference in production technique the active pore area of the 0.2 micron tube is only expected to be $(0.2/0.5)^2 = 0.16$ of the area of the 0.5 micron tube. This observation correlates with the flux reduction of about 90% for 0.2 micron tubes compared with 0.5 micron tubes.

The manufacturer developed a technique he calls "hyperizing" in conjunction with his interest in non-membrane filtration. The technique produces a very thin layer of small powder deposit on a larger pore substrate, thus achieving a small pore surface without diminishing the active surface area.

Six of these special tubes were evaluated during formation in pairs to determine the resulting membrane performance as compared with the performance on the earlier tubes. The data are collected in Table 10 for each of the trials. Included in the table are the average expected performance levels for tubes nominally 0.5 micron, the results of one reused hypertube, and the result of a standard tube formed concurrently with the hypertube. No carbon filter aid was employed. The first pair of tubes produced only average rejection although the flux was reasonably high. The zirconium step was of long duration (seven hours). The second pair of tubes also did not produce good rejection presumably due to a sudden pH increase which sometimes occurs during formation due to procedural difficulties. The third formation pair included a previously-used tube which had been cleaned in acid and baked. The fourth formation included a 0.5 micron tube which also had been baked with the hypertube.

The average flux of the formations on the hyperized tubes was 1.75×10^{-5} m/sec, slightly larger than that expected for 0.5 micron tubes due largely to the one individual high value. The relatively low rejection values are not considered to have a significant effect on the flux levels observed. Therefore, it is concluded that formations on "hyperized" tubes did not result in significantly higher fluxes compared with experience on 0.5 micron tube supports.

Table 10. EVALUATION OF MEMBRANE PERFORMANCE ON SPECIAL TUBES

Tube	Pressure (MN/m ²)	NaNO ₃ Solution (mg/l)	pH	Conductivity Rejection (%)	Flux (m/sec)
Old average	1000	-	-	85.0	1.4 (-5)
1	970	4250	6.7	40.0	5.8 (-5)
2	970	4250	6.7	47.0	2.1 (-5)
3	975	3820	7.2	52.0	0.4 (-5)
4	975	3820	7.2	52.0	0.7 (-5)
One of above	900	3820	8.2	87.2	0.7 (-5)
5	900	3820	8.2	87.2	0.6 (-5)
Regular	875	3820	6.8	72.0	1.8 (-5)
6	875	3820	6.8	77.0	0.9 (-5)

Temperature about 50 - 60°C.
Velocity = 2 m/sec.

4.0 CONCLUSIONS

(1) The use of stainless steel as a support material for dynamic membrane formation has been demonstrated.

(2) Flux declines occurred over the entire ninety-day test period, subject to flux increases associated with lower feed concentrations. These declines must be considered in the design of the system control scheme.

(3) No significant losses in membrane solute rejection were associated with the extended operation.

(4) A membrane on stainless steel ranked high in both flux stability and solute rejection.

(5) One-pass filtration is expected to suffice for meeting all water requirements except ammonia and foaming. Multi-pass filtration will improve these qualities, but the reduction in urea concentration to preclude ammonia production may be impractical.

(6) Hypochlorite may be used effectively to remove urea and ammonia from shower water. Excess hypochlorite may be decomposed by the use of cobalt or $\text{Co}(\text{OH})_2$.

(7) The calculated optimum operating conditions for the dynamic membrane extend to low velocity, a temperature of near 75°C , and recovery rates adjusted to enter the VCD with the fluid concentrate.

(8) A breadboard item was fabricated and the membrane was formed twice having goal rejection and flux. The method of manifolding multiple tubes suffered from design deficiencies which prevented fluid cross-over between channels. The module was never successfully operated as planned due to the mechanical problems. There was no indication that any problems existed with either the membrane or its support tube.

(9) Formations on "hyperized" tubes did not result in significantly higher fluxes compared with experience on 0.5 micron tube supports.

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APPENDIX A

PARAMETRIC TEST OF A Zr(IV) OXIDE-POLYACRYLIC ACID DUAL LAYER
HYPERFILTRATION MEMBRANE WITH SPACECRAFT WASHWATER

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ABSTRACT

Performance data consisting of solute rejections and product flux have been measured, as dependent on the operation parameters. These parameters and ranges were pressure ($5 \times 10^6 \text{ N/M}^2$ (750 psi) to $7 \times 10^6 \text{ N/M}^2$ (1040 psi)), temperature 347°K (165°F) to 368°K (200°F), velocity (1.6 M/sec to 10 M/sec), and concentration (up to 14x). Tests were carried out on analog washwater. Data taken include rejections of organic materials (TOC), ammonia, urea, and an assortment of ions. The membrane used was a dual layer, polyacrylic acid over zirconium oxide, deposited in situ on a porcelain ceramic substrate.

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1.0 SUMMARY

A membrane technology using zirconium oxide followed by polyacrylic acid layers has been developed by the Oak Ridge National Laboratory. In 1972 engineering personnel at Clemson University applied this technology on a feasibility test basis to the reclamation of potable water from washwater for NASA. The present contract extends the earlier work to determine the effects of basic operating parameters on the performance of the membrane.

A test rig was designed and constructed which would be capable of operation in the intended range. Basically a unit with 70 atmospheres pressurization at 80 liters per minute of near-boiling-temperature water was provided. The minimum operating volume was just under 10 liters and the maximum volume about 200 liters. Washwater was generated and stored in accordance with an established procedure which uses shower water and clothes wash from test subjects supplemented by the addition of deficient chemicals.

The test was executed in two portions. In the first portion the effects of pressure, temperature, and velocity were separately determined. The flow arrangement was configured to permit a small portion of raw feed to mix with recycle concentrate to form the fluid exposed to the membrane. Standard conditions of pressure = $6.8 \times 10^6 \text{ N/M}^2$ (950 psi), temperature = 348 K (75C), and velocity = 7.7 M/sec were selected. While maintaining other parameters constant with loop concentration approximately 2.4 times feed concentration, each operating parameter was varied from its standard value. Pressures from $5.27 \times 10^6 \text{ N/M}^2$ to $7.24 \times 10^6 \text{ N/M}^2$ (750 to 1040 psi), temperatures from 348K to 366K (75C to 94C), and velocities from 1.5 to 7.7 M/sec were observed.

The second test portion comprised the concentration variation. The flow arrangement was configured to route all recycle concentrate to mix with the feed reservoir. Simple mass balance theory shows this configuration to be equivalent in operation to a long once-through membrane. A batch representing ten men-showers was processed 93 percent to completion while operating at the standard test conditions. Further processing was limited by the minimum operating volume to insure full flow to the pump suction.

Conductivity and product flow rate data were taken regularly and pH measured infrequently. Small samples (about 100 ml) were sent to a local contractor for C.O.D. analysis. Large samples (about 1 liter) were shipped to NASA Houston for analysis. The primary items of importance were initially considered to be organic carbon materials, ammonia, and urea. Results of the testing showed the feed ammonia content to be larger than anticipated so that ammonia is clearly the most difficult solute to reduce to acceptable levels. A single filtration recovering 93 percent of the feed resulted in an averaged product ammonia content of 6.5 mg/l from feed levels of 24 mg/l. Based on this observation a product-recycling system would reduce the ammonia content to below 1 mg/l in less than three passes. The product thus produced would contain very small quantities of organics and acceptable amounts of urea in addition to traces of other solutes.

The results generally were near those previously experienced during the feasibility demonstration in 1972. However the urea rejection was found to be substantial (about 60 percent) rather than the low (about 10 percent) level heretofore determined. No explanation for this is advanced. However the urea molecule is anticipated to be excluded on the basis of its molecular weight rather than by ion exclusion. Comparison with other non-ionized molecules having molecular weights of the order of 100 indicate that a 60 percent rejection is not unreasonable.

One important test point at the lower velocity extreme was marred by the conjunction of two phenomena. At the time when the low velocity points were being run, a second feed batch was introduced which had markedly different pH. A decline in performance was registered and it is not possible to conclusively separate the effect of new feed and low velocity. However it is deemed most probable that the low velocity was not responsible for the performance decline. Further testing is recommended to permit proper evaluation.

2.0 INTRODUCTION

Beginning in 1965 researchers at the Oak Ridge National Laboratory (ORNL) began to evaluate the solute separation potential of hydrous metal oxide semi-permeable membranes. In 1969 it was determined that a dual layer membrane formed of zirconium oxide and polyacrylic acid had improved lifetime and solute separation potential. During the following period ORNL explored the application to seawater, brackish water, and to various waste streams. In 1972 Clemson University applied the membrane to spacecraft wash-water under contract to NASA-Langley. This application was considered promising due to the properties of the membrane which allow high temperature operation (347°K and above) and good performance for relatively low concentration solutions. The product water from a batch of processed shower water met the accepted standards for potable water. Based on this favorable result NASA has elected to evaluate the effect of various operational parameters on the flux and rejection properties of the dual layer ZrO-PAA membrane.

3.0 CONCLUSIONS

The membrane evaluation was executed according to plan with the following essential results achieved. The rejections of various solutes are not strongly variable with pressure, temperature, velocity, or concentration in the range tested. Temperature above 358°K resulted in slight declines in rejection, while velocity below 3 M/sec apparently resulted in a larger performance decline. The velocity variation is important to the designer to enable rational decisions on pump requirements and system configurations, but the long term effects associated with low velocity (not studied herein) are probably more important in this respect. The velocity effect was masked by conjunction with a change in pH so that no strong conclusions can be made.

Rejections of important solutes were determined to be

Total Organic Carbon	96%
Ammonia (NH ₃)	80 to 90%
Urea	60%

Other solute rejection and feed concentrations are such that product water concentrations are well within potability limits. The ammonia rejection appears to be determined to a relatively large uncertainty though all procedures indicate higher accuracy should have been attained.

A batch of washwater was processed 93 percent toward completion to determine the effect of concentration. The laboratory system minimum volume prohibited further processing. The calculated value of mixed product concentration compared to feed in ppm is as follows.

	<u>Feed</u>	<u>Mixed Product</u>	<u>Allowed Maximum Level</u>
TOC	180	37	100
Urea	64	50	50
NH ₃	24	6.5	1

From this it is apparent that NH₃ is the critical solute, and consequently that a multistage system is likely to be required.

4.0 RECOMMENDATIONS

The primary results obtained herein should be utilized in a design optimization of a hyperfiltration system. The design effort should be flexible enough to accommodate a range of tube sizes. The effect of not yet determined, long-term results of low velocity exposure should be treated in an appropriate manner. This study will result in an ideal goal system which assures minimum total weight penalty - valid for any of several tube sizes.

The long-term effects on performance should be studied experimentally. A life test should be conducted during which the effects of velocity at relatively high concentration may be documented. Also the effect of fresh feed additions on membrane performance, particularly flux, may be documented.

Consideration should be devoted to the problem of the substrate mechanical support. The use of the desirable inside pressurization will require a different tube than that used in the present program. Tubes employed in this program, pressurized on the outside, may prove acceptable in performance and are expected to be adequately strong. Fabrication of elementary support arrangements should be carried out to allow laboratory evaluation of basic performance.

It is suggested that the effect of feed pH on rejection of solutes, particularly NH_3 and urea, be determined. A re-examination of low velocity conditions at perhaps even higher concentration should also be conducted.

5.0 TEST DESIGN AND CONDUCT

5.1 Description of Objectives

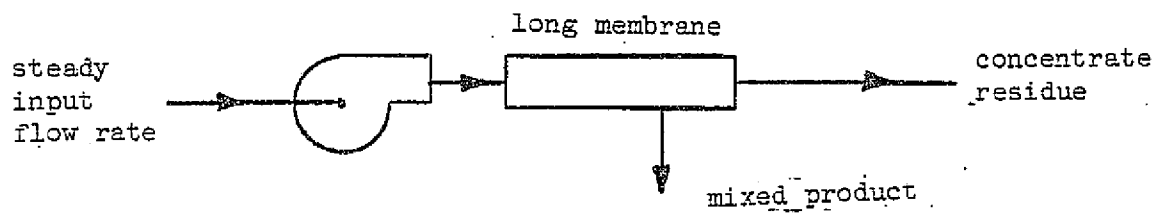
The object of the work reported herein was to determine the effect of certain operating parameters on the performance of the hyperfiltration membrane under consideration when operating on washwater. The parameters are pressure, temperature, velocity, and concentration. It is normally conceded that the pressure will be of the order of 60 atmospheres, as generally higher quality product water is achieved at higher pressure. The temperature of the stored shower water was anticipated to be 347°K for sterilization, and the range of the test data was anticipated to cover the range from 347°K to near boiling. Velocity was expected to be important over both short and long time scales. The short term effect is due to concentration polarization, which describes the rise in concentration level at the membrane over that of the mainstream flow. The concentration polarization is velocity dependent because the level of concentration near the membrane is inversely proportional to the rate of diffusion from membrane to free stream which is in turn nearly proportional to velocity. Concentration polarization was expected to become noticeable at 2 M/sec and to be severe at 0.3 M/sec.

The long term effect of velocity is not clearly understood, but generally is referred to as fouling or scaling. First, in the supersaturated solution, the increased concentration at the membrane caused by a reduction in velocity produces faster deposition of solute. This type of fouling, which includes that type called scaling, may occur. Second, there may be materials in suspension which, at low velocity, may be deposited on or attracted to the surface of the membrane. Any such materials would tend to remain on the membrane by virtue of the flux being withdrawn and by the pressure of the water passing through it. Particularly the immiscible liquids are considered candidates for such action in that they could spread enormously under the influence of pressure and shear after initially contacting the membrane. Third, there could be erosion or modification of the membrane material itself. This effect would possibly be reduced at lower velocities.

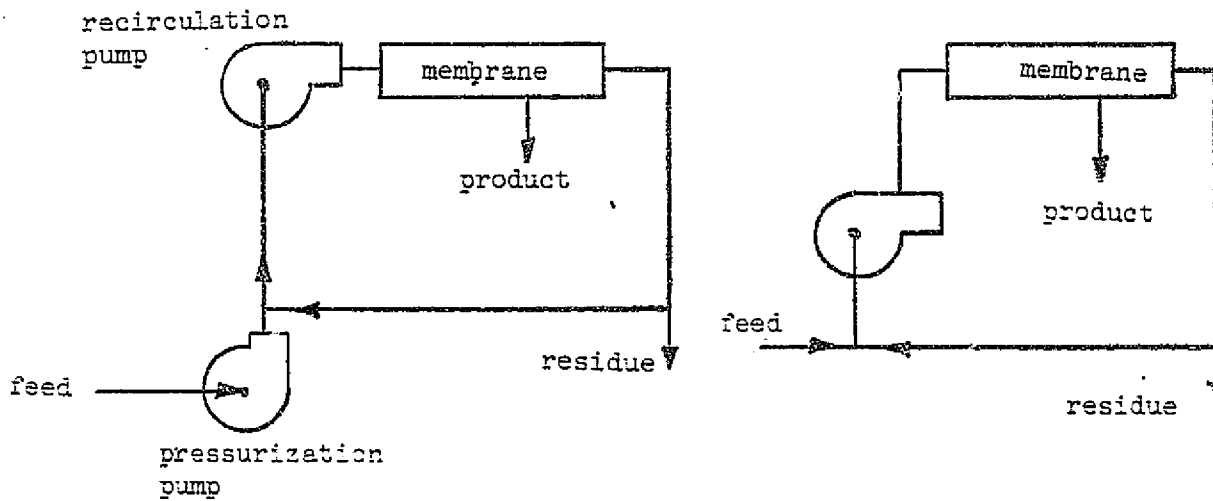
In addition to pressure, temperature, and velocity effects, it was anticipated that solute concentration may affect membrane performance. The rejection of ion-exclusion membranes is highly dependent on concentration whereas for ultrafiltration membranes rejection is less dependent on concentration, for solutes in ionic bonded forms. Experience with washwater gained in earlier testing indicates that organic substances (measured by TOC or COD) are rejected almost equally or perhaps even increasingly with concentration. The rejections of NH_3 and urea, other important substances, are also not strongly affected by concentration.

5.2 Prospectus

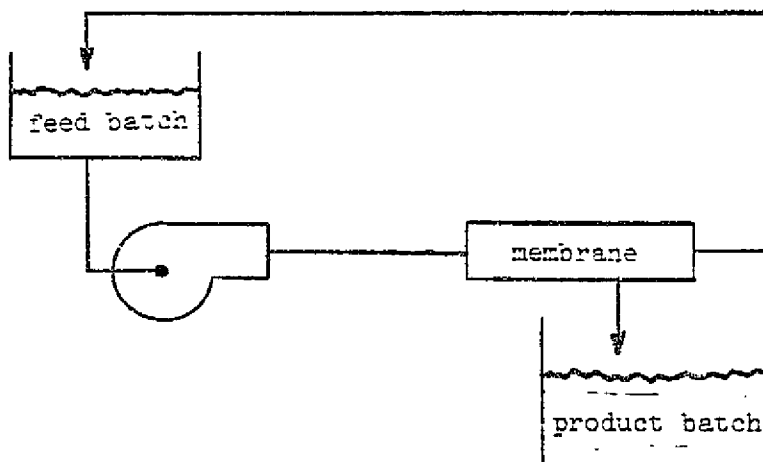
Hyperfiltration membranes can be utilized in any of the basic single stage schemes shown in Figure 1. In the first feedwater is fed at a constant rate into a module configured to allow the recovered product and residual concentrate to exit. This "once through" arrangement is different from the second scheme shown (Figure 1b) which recirculates most of the loop fluid while withdrawing a



1a. Once-through Arrangement



1b. Recirculating Arrangements



1c. Batch Processing Arrangement

Figure 1. Typical Single Stage Arrangements

desired ratio of loop flow to the product flow. The third scheme is a batch process in which the loop fluid includes the feed reservoir. The process continues until the desired recovery fraction of the original fluid has been processed as product water.

Appendix A presents a simple analysis of these various flow arrangements using a hyperfilter. The analysis presented there shows that the batch process and the once-through arrangement are equivalent and are favored over a recirculating type system.

Based on the feed analysis of Reference 1 it is deemed feasible that a single stage system could suffice. However, based on results shown herein, the feed is more contaminated with NH_3 than anticipated so that multistage filtration is required. The requirement of multistage filtration leads to greater energy consumption and possibly some increase in complexity and weight. The conclusion of above that the once-through or batch process is superior to recirculation carries over to the multistage concepts.

While the use of a recirculating system is not anticipated for a flight article, such a system is useful in the laboratory. For, when operated at proportionate concentration, it may be maintained to within a close tolerance over an extended time. Thus one may effectively insure constant concentration while varying temperature, and other parameters. In addition any suspected performance variation may be examined by restoration of conditions to determine the occurrence of irreversible changes. Because of these advantages a recirculating system was used to determine the effects of pressure, temperature, and velocity. Then a batch of shower water was processed in escalating concentration simulating the individual points of a once-through filtration arrangement.

While the use of the steady-state recirculation arrangement allows the loop concentration to remain essentially unchanged during other parametric variations there is a slight skewing of the relative concentration of the various solutes since rejection on each is different. For example, suppose solutes 1 and 2 are rejected with different efficiencies, and then compare a once-through arrangement and a steady-state arrangement. At the position in the once-through arrangement where the concentration of solute 1 is identical with that of solute 1 in the steady-state arrangement, the concentrations of solute 2 are not identical in the two arrangements. By use of concentration analysis, presented in Appendix A, one may determine that relative abundance is effectively independent of flow arrangement in the concentration range associated with the parametric tests.

5.3 Test Apparatus Design

5.3.1 Design Considerations

Test hardware design was largely determined by the choice of the membrane support tube. The Selas single-nole tube or seven-nole tube having 0.27 μ pore size was selected. Use of this support precluded the use of filter aid or other composite form of support. Also, the benefit of inside-out product flow

direction allowed the flow regime which is the most easily understood, that of tube flow. Having chosen the support (dictating flow area) and selected 7 M/sec to be a required velocity, a pump flow rate of 8 l/min at high pressure (60 atmos) was estimated. All pump makers surveyed indicated that their 8 l/min unit was the same hardware as a larger unit, typically 150 to 400 l/min. An approximately 80 l/min pump was purchased, the selection based on other considerations. To fully utilize this flow rate it was determined that the use of a membrane formed of multiple tubes in parallel would lead to faster data production. However, we were not successful in operating a multiple tube arrangement and the test was performed on a single seven-hole tube ceramic support.

5.3.2 Detailed Design and Materials

Experiments were conducted utilizing a single pump pressurization-circulation system shown schematically in Figure 2. Feed is taken from an elevated tank which maintains the net positive suction head required by the pump. Pressurized feed flows either through the module, a pressure reduction valve and flow indicator, or through a pressure reduction valve in the by-pass line. By-passed feed and concentrate re-join and the stream is directed either to the suction of the pump or to the feed tank by a 3-way valve. Heat generated by the pump is removed by a concentric tube heat exchanger using tap water coolant in the annulus.

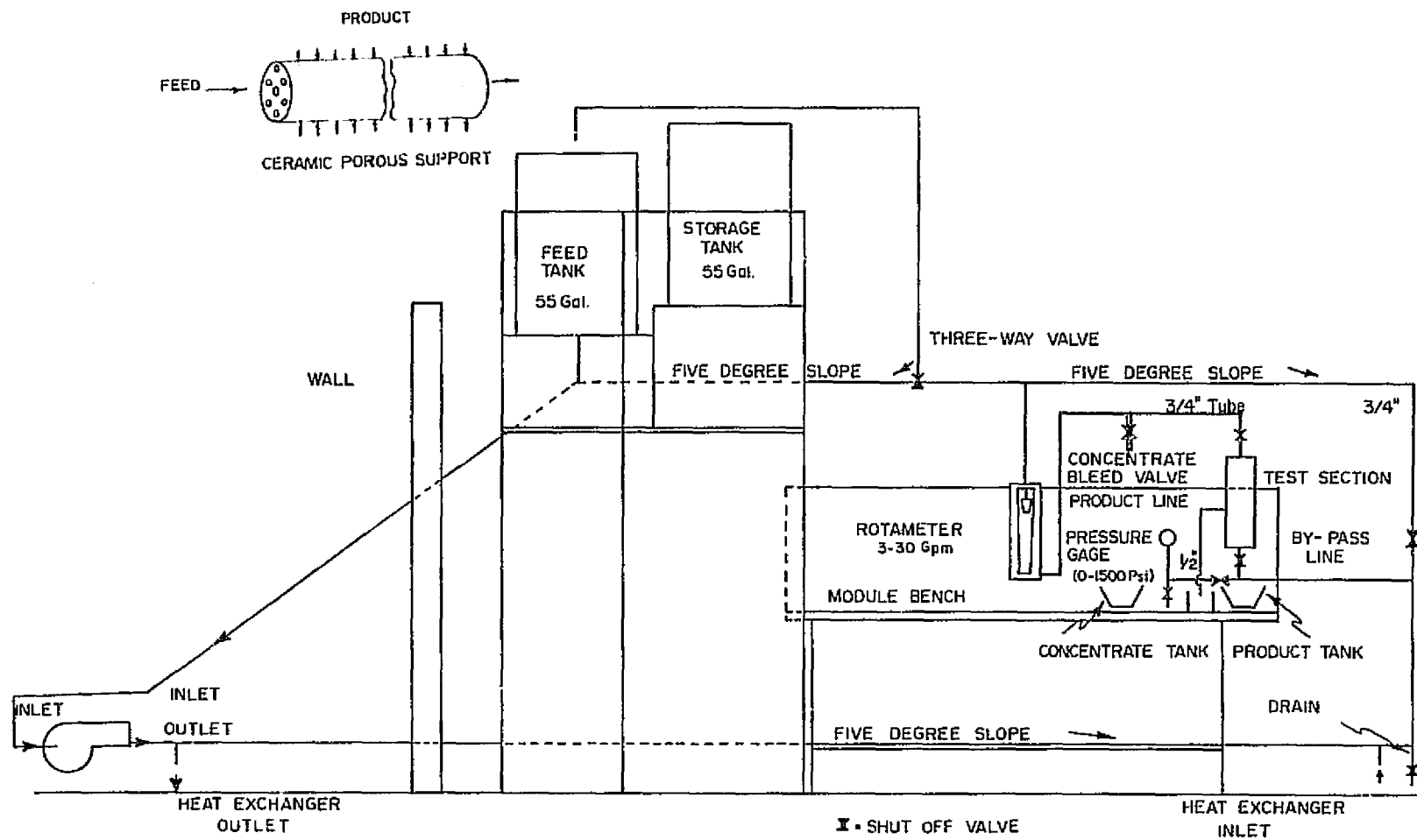
Resistance to corrosive attack of chemicals used in cleaning of the system, formation of the membrane and by the feed itself is required when selecting wetting materials (see page 14 for wash and formation technique). Though the system must withstand the feed and wash solutions with a minimum of structural attack, prevention of contamination of solutions used in membrane formation is critical to good membrane quality and largely determines the materials selected.

Relying on previous experiences at Clemson University and ORNL, the basic metal chosen was series 300 stainless steel. The locations and types of materials used throughout the wetted portion of the system are given in Table I.

The pump chosen was a Sunflo single stage, high speed centrifugal, model P2CHB manufactured by Sunstrand Fluid Handling, Denver, Colorado. The pump is constructed of type 316 stainless steel with a tungsten carbide and carbon rotary seal. Stationary seals of teflon were used throughout.

One and one-half inch diameter 316 stainless steel pipe with a flex joint of natural rubber was used between the elevated feed tank and the suction of the pump. Stainless steel tubing with Swagelok fittings and valves was used throughout the rest of the system. Tygon tubing is used to return product to the feed tank and for other temporary transportation of fluids from or to storage. The three 55-gallon feed and storage tanks are constructed of type 304 stainless steel.

Pump protection was furnished by switches which deactivated the system when feed tank level dropped below a certain level, or when pump discharge manifold temperature exceeded a set level (normally 90°C). Successful membrane formation was accomplished utilizing the single 7-hole tube module shown in Figure 3. This module was used for all tests. The individual channel diameters are 2 mm,



SCALE	TEST SYSTEM
1" = 1.5'	NASA PROJECT

Figure 2 System Schematic Diagram

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Table I . Type and Location of Wetted Materials

Component	316 S. S.	304 S. S.	Buna-N	Viton	Tungsten Carbide	Carbon	Teflon	RTV Rubber	Natural Rubber	Glass	3603 Tygon	Ceramic
Pump	X				X	X	X					
Rotameter	X		X							X		
Piping	X								X		X	
Valves	X											
Tanks		X										
Switches	X											
Pressure Gauge	X											
Module	X		X					X				X

and the length is 35 cm. Thus, the total membrane active area is approximately 156 cm^2 , requiring a flow of 13.6 liters per minute to provide 10 M/sec velocity.

5.3.3 Instrumentation

During operation certain parameters were monitored to evaluate membrane performance. These parameters with the instrument or method used and accuracy are given in the table below.

PARAMETER	INSTRUMENT OR METHOD	ACCURACY
Module inlet pressure	Heise ¹ (0-1000 psi) bourdon gauge	±2%
	Wika ¹ (0-1500 psi) bourdon gauge	±2%
Feed temperature	Barber-Coleman 16 point	±1°C
	Recorder w/Cu-Cn thermocouples	
Feed flow rate	Brooks Rotameter ² 1110A-12H5BLA	±2% FS
	3-30 GPM	
	Brooks Rotameter ² 1114-09H3BIA	±2% FS
Conductivity	0.3-3 GPM	
	Balsbaugh	±2% FS
pH	Type 100 conductivity bridge	
	International Biophysics Corp.	±0.1 unit
Product flow rate	Model 180-001 pH meter	
	Graduated cylinder and stop watch	±3%
System volume	Calibrated dip-stick	±0.25 l

¹ calibrated by dead weight tester

² calibrated by stop watch and scales

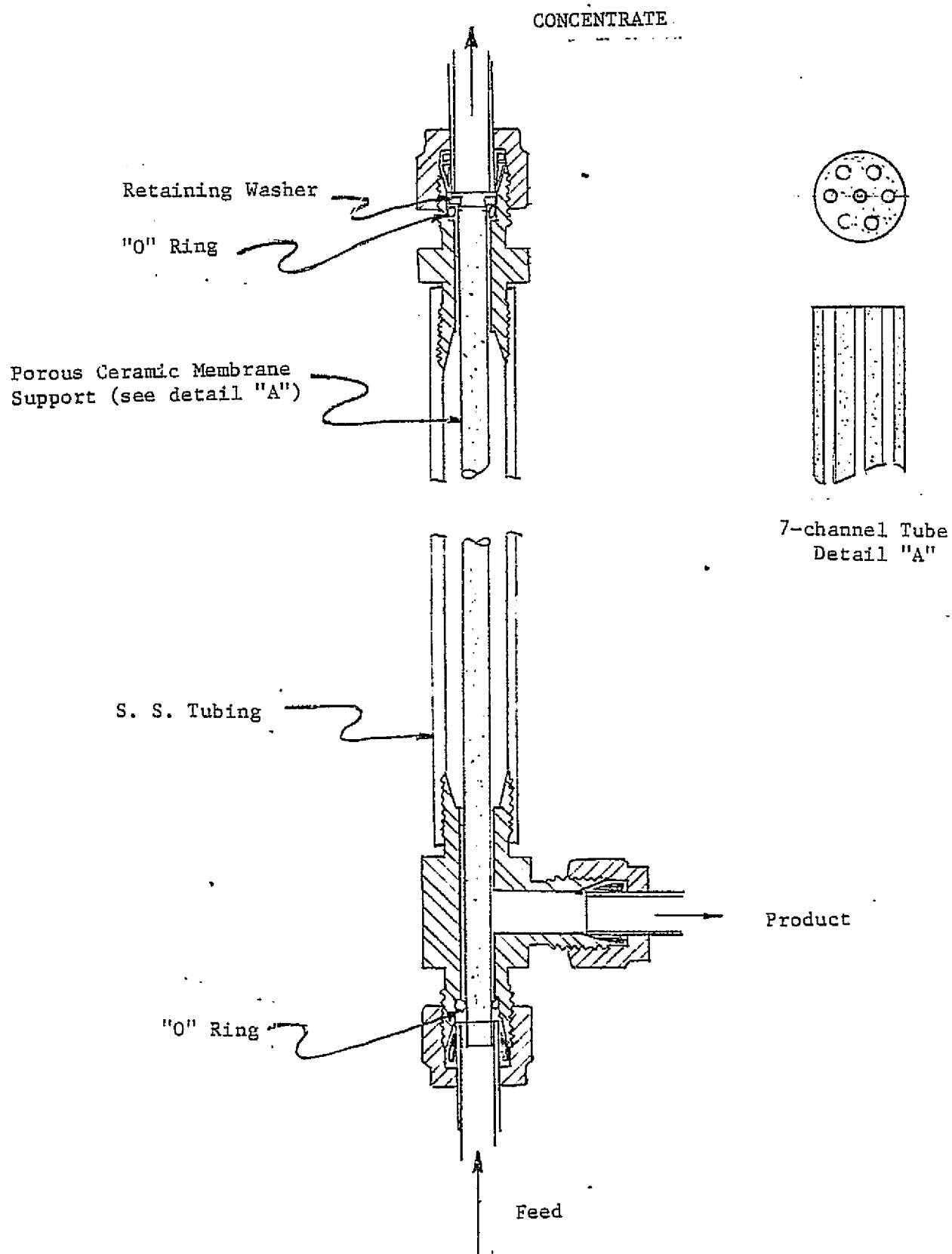


Figure 3

HYPERFILTRATION MODULE

5.4 Membrane Formation

5.4.1 System Wash

The system must be thoroughly cleaned before membrane formation is attempted. A one molar NaOH wash circulated at high velocity followed by a one molar HNO₃ wash, each one hour long, has proven adequate in most cases. If the system is severely contaminated the temperature can be raised to 60°C during the acid wash. The base-acid wash is followed by three or four drain and fill cycles during which all stagnant regions of the system are flushed. The system is then drained.

5.4.2 Formation

The module housing the membrane support is piped into the system and isolated by closing the up-stream and down-stream valves. The cleaned system is filled with a known quality of decontaminated water. (Permeate from a U.O.P. spiral-wound module with tap water as feed was used in our test.) The appropriate amounts of ZrOCl₂·8H₂O and NaCl are added producing a 10⁻⁴ molar and 0.05 molar concentrations respectively. The pump is then turned on with all flow passing through the by-pass and the pH is adjusted to 4.0 plus or minus 0.2 by adding HCL or NaOH. The circulating fluid is introduced to the module gradually until the required velocity and pressure are achieved, usually 5 M/sec and 65 atmospheres. Conductivities of the feed and product are monitored until rejections reach 30 to 40%. If rejections do not reach this level in a reasonable length of time additional zirconium oxy-chloride can be added to double or triple the zirconium concentration.

The pH is adjusted to 2.0 and 50 ppm polyacrylic acid (PAA) is added and the solution is circulated past the support for 1/2 hour. The pH is raised to 3.0 and circulated for another half hour. This process is repeated in unit increments to a pH of 7 or 8 and the membrane is considered formed. At this point the conductivity rejection should be greater than 90% and the flux between 0.1 and 0.4 cm/min.

5.4.3 Regeneration

If rejections are considered unacceptable at the end of the formation, or if the performance has declined, a regeneration can be attempted. The pH is reduced to 2.0, PAA is added, and the pH is raised in unit increments of 30 minutes duration to a pH of 7 or 8. PAA may be added in amounts from 0 to 50 ppm for this procedure, with a full 50 ppm addition being normal. This usually results in a higher rejection and lower flux.

5.4.4 Re-use of Substrate Tubing

No reliable methods were determined which will allow the chemical removal of the residue of membrane from the support. The type of tube used in this test is no longer in production, and only a limited number were available. Therefore in reusing the tubes, they were fired in an air atmosphere furnace to 700°C for 2 to 3 hours to remove the residue. This procedure provided tubes which had the same permeability as new tubes. No serial record of tubes was kept to determine the effect of re-use on performance. However no irregularities in tube performance that might be ascribed to the firing process were generally observed.

5.5 Summary of Operations

Appendix B is a table which summarizes the activity during the performance of this work. Some seventeen membranes were attempted. Many of these failed due to fracture of the ceramic support. Others exhibited inferior performance and were discarded. Finally others were formed and stored as insurance in case of further tube fractures. These were extant at the test end.

Figure 4 shows the time line during the parametric test of 1 through 3 July 1974. This test began with the production of 14 liters of product to establish an initial elevated concentration level. After the desired concentration level was reached, concentrate was released at a rate of 3 units concentrate per 5 units product. This ratio was designed to hold the solute concentration essentially constant. The test proceeded through pressure and temperature variations to the 96°C temperature level at which time the pump lost suction. Upon restart and stabilization at 93°C a test point was completed. The loop was then shut down briefly for changeover to a smaller flowmeter. Approximately 2.2 liters of concentrate were lost during this maneuver, requiring operation with zero concentrate removal for a period to regain the desired concentration level. At a point 90 percent through run 9, the feed supply was consumed, and additional feed, not identical to that previously used, was administered. Run 10 continued on this second feed batch.

After a brief start on the concentration run which followed the parametric runs (1-10), we experienced a pump seal failure and terminated further activity. Upon repair and resumption of activity the concentration run was performed to about 93 percent recovery of initial feed volume. The same membrane was used in both the parametric and concentration tests.

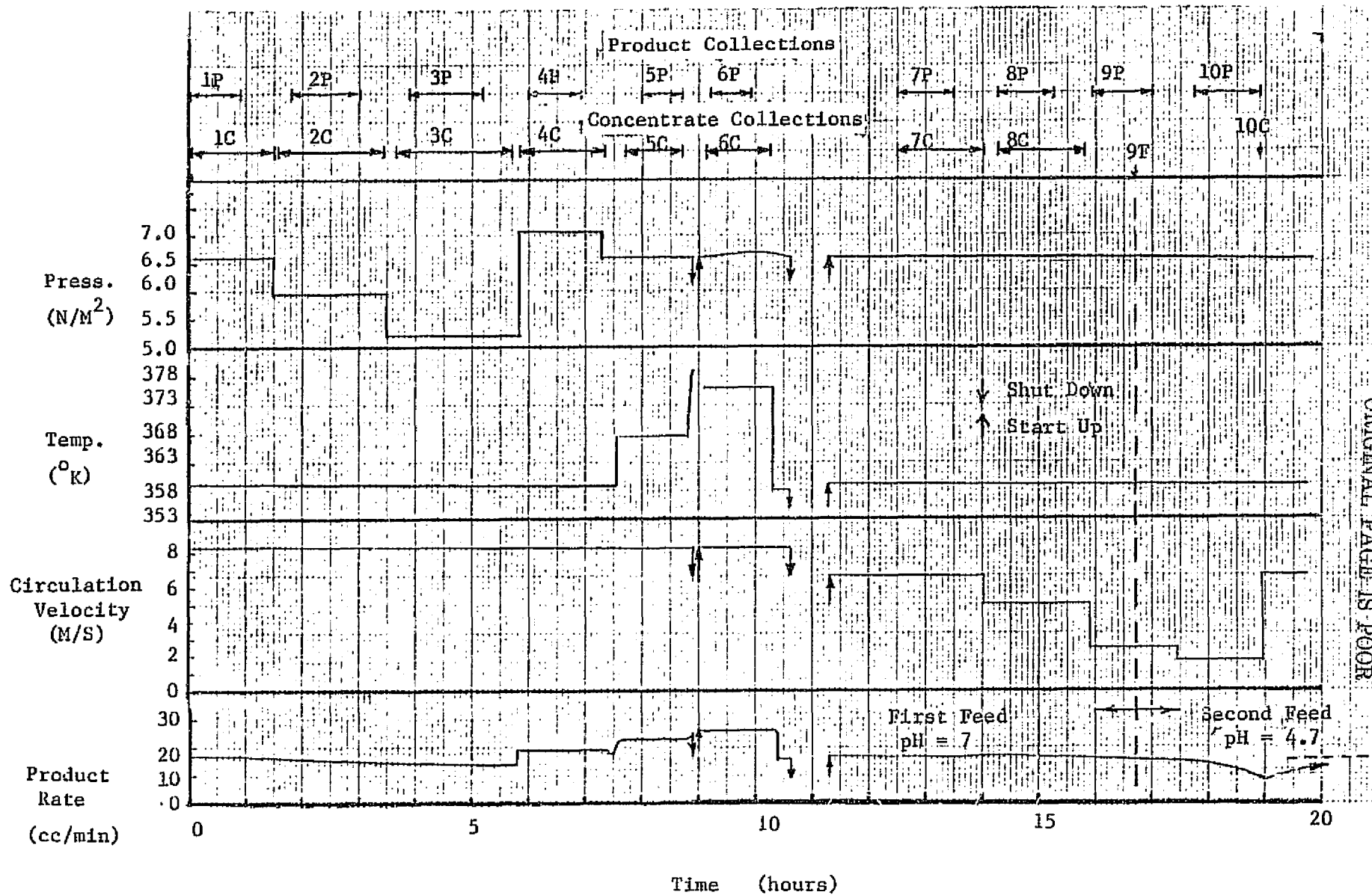
Upon receipt of the pre-treated urine from Houston we evaluated the membrane performance to be lower than desirable and prepared to remove and replace the membrane and its support. Inspection revealed a large quantity of lint which had clogged the inlet end of the tube nearly to complete closure (visually). Reasoning that the reduced performance could be due to the almost certain reduction of pressure caused by the obstruction, the cleaned tube was retested. However, no significant performance increase was immediately registered and a new membrane was added.

The urine run was initiated and carried 30 percent to completion at which time the pump seal leaked forcing shutdown due to loss of fluid. The seal failure was not identical to that previously experienced and also was not due to a factor obvious upon inspection.

6.0 DISCUSSION OF RESULTS

6.1 Data Analysis Procedures

The pressure, temperature, and velocity parametric data were observed during a 19 hour period. The major events were chronologically related as indicated in Figure 4, which shows the pressure, temperature, velocity, product flow rate, and collection periods for the samples. Immediately prior to



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Figure 4 . Major Event Chronology During Parametric Tests

the period covered by this plot, the test facility had been operated with only product flow withdrawn to increase the loop concentration. Some 14 liters of product were withdrawn, producing a concentration factor of about 2.4 in the 10-liter active loop volume.

During the entire 19 hour test period, concentrate was withdrawn from the circulating loop at 60 percent of the product flow rate. The withdrawals of concentrate were made at 15 minute intervals, approximating continuous outflow. Thus, the collection interval for concentrate samples was 66 percent longer than the respective collection interval for product samples. Collection of product water was generally delayed long enough to allow the "old" product to be purged from the system volume between the sample port and the membrane. Experience gained during system checkout had indicated that about 100 ml. of product would insure the purge of the "old" product.

A short interruption in the continuous operation of the test occurred between sample numbers 5 and 6, due to a temperature over-shoot resulting in the loss of pump suction. A longer shutdown occurred preceding point 7 when a change to a smaller flowmeter, required for the low velocity runs, was made. The loss of water during this equipment change required a reconcentration period of over one hour during which only product was withdrawn from the system. Near the end of the collection of the sample number 9, a new batch of feedwater was added to the system reservoir. This batch of feedwater was not identical to the first, resulting in some difficulty in interpretation of test results.

The data taken for each sample are shown in Table II. These data are primarily the result of analysis conducted at NASA-JSC, with some results obtained on line at Clemson, the C.O.D. by a local contractor. Accuracy of analysis are as indicated in Appendix C for the samples taken. Many of the feed and concentrate samples are difficult to extract a representative sample from, and production of filtrate was extremely difficult. An internal consistency check of C.O.P. with T.O.C. should be that T.O.C. multiplied by a molecular weight ratio (about 2.7) should be equal to or greater than the C.O.D. level. (Greater than because of constituents which do not oxidize with potassium dichromate; for example, urea.) As noted, the data do not afford a universal check according to this criterion. It is believed that the C.O.D. procedure yields greater accuracy if the result is known a priori, or at least if a realistic upper bound can be established. Thus the repeated tests for C.O.D. have the benefit of hindsight and therefore are more accurate.

Internal consistency of the data may also be examined, using mass balance of the various solutes. An attempt at depicting this is shown in Figure 5 for NH_3 and T.O.C. The mass balance can be used to determine the product concentration which would yield the measured concentrate concentration with the measured feed. Such a procedure is impractical due to the magnification of the concentrate variation on the predicted product concentration. For example, a ten percent variation in concentrate concentration between successive samples implies about a one hundred percent variation in product concentration. However, the measured product concentration can be used to critique quite effectively the concentrate and even the feed concentration values, as follows. The T.O.C. loop concentration at the beginning of the test should have risen from 124 (feed concentration) to about 283 at an average rejection rate of 0.95, using

Table IIa Analysis of samples for
selected Solutes

Run	Conc(C) or Prod(P)	Press (10^{-4} xN/M ²) (psig)	Temp (°K)	Vel (m/sec)	Cond. (μmho/cm)
	FEED FOR RUNS 1 - 9 2/3				530
1	C	950	349	7.7	1750
1	P	668	349	7.7	140
2	C	850	349	7.7	1800
2	P	597	349	7.7	170
3	C	750	348	7.7	1800
3	P	527	348	7.7	180
4	C	1040	348	7.7	1700
4	P	724	348	7.7	150
5	C	950	358	7.7	1900
5	P	668	358	7.7	195
6	C	668	366	7.7	1900
6	P	668	366	7.7	230
7	C	668	350	6.1	1980
7	P	668	350	6.1	185
8	C	668	350	4.5	2050
8	P	668	350	4.5	200
9	FEED FOR RUNS 9 2/3 - 10				660
9	P	668	349	2.3	220
10	C	668	349	1.5	1600
10	P	668	349	1.5	190
11	C	668	349	2.3	870
11	P	668	349	2.3	84
12	FEED		349		640
12	P	668	349	7.7	57
13	C	674	346	3.0	905
13	P	660	351	3.0	120
14	P	668	351	3.3	160
15	P	668	352	3.0	285
16	P	674	352	3.0	485
17	P	671	351	3.0	660
18	P	674	351	2.8	750-800
20	C	-	-	-	-
22	C	-	-	-	-

Table IIa Continued

TOC (ppm.)	COD (ppm.)	NH ₃ as N (ppm.)	Urea (ppm.)	pH	Inorganic Carbon (ppm.)
124	-	24	36	6.44	16
260	657	77	90	6.47	25
8	90	9	19	7.35	8
257	828/475	72		6.64	27
12	100	7	21	7.20	9
245	657	59	69	6.35	27
7	109	8	18	6.69	12
244	600/375	64		6.36	26
10	81	7	15	7.17	10
244	486/359	60	55	6.37	25
10	90	8.2	18	6.65	12
275	1000	60		6.42	20
26	67/33	8	15	7.00	6
260	847	59	50	6.33	25
11	84/42	7	15	6.47	10
324	419/481	77		6.38	16
10	19/44	7	12	6.5	12
121	--	33	58	6.69	39
17	44/33	9	18.5	6.59	8
190	438	25	55	6.16	20
14	--	13	40	7.28	15
212	552	17		8.47	13
20	19/22	3	46	9.08	7
183	1066	31		6.92	27
25	50/54	.6	46	7.13	6
203	1485	25		6.68	17
36	124	5	50	9.28	7
36	129	5	75	9.37	8
60	185/185	7	63	9.38	17
77	257	26	55	8.88	17
70	257	18	55	6.51	20
128	294/244	16	72	8.82	12
4421	--	82	255	7.5	29
3673	10,728	85	230	7.5	27

Table IIb. Complete Analysis of Selected Samples

Determination	12(Feed)	13P	15P	18P	20C	1F	3P	5P	7P	9P	11P
Chromium as Cr^{+6} , ppm	100			1	1000	100					
Silver as Ag, ppm	.01			.01	.058	.017					
Zinc as Zn, ppm	.54			14		.34					
Fluoride as F, ppm	.04			.066	.275	.28					
Nitrate as NO_3 , ppm	2	.2	.2	.69	.49	.75	.41	.25	.2	.38	.26
Sulfate as SO_4^{-2} , ppm				8	4000	45					
Chloride as Cl, ppm	192	16	49	190	1700	221	24	48	39	45	6
Conductivity (umho/cm)	640	120	285	750	---	1750	180	195	185	220	84
TOC, ppm	183	36	60	128	4421	124	7	10	11	17	20
COD, ppm											
NH_3 , ppm	31	5	7	16	82	24	8	8.2	7	9	3
Urea, ppm	44	50	63	72	255	36	18	18	15	18.5	46
pH	6.92	9.28	9.38	8.82	7.5	6.44	6.69	6.63	6.47	6.59	9.08
Inorganic Carbon, ppm	27	7	8	12	29	16	12	12	10	9	7

for example equation 2 of Appendix A for predictive basis. The loop concentrations were measured at 240 to 270 for the most part, (run numbers 1-7) indicating by the strength of several measurements that the feed reading tended to be high by perhaps 10 ppm. So the feed could actually have been about 115 ppm rather than 124 based on this observation. Assuming that run 1 started either at 250 or 270 (T.O.C.), that the feed analysis was incorrect by the aforementioned amount, and that the product concentrations are known without error, the curves of Figure 5 are determined. Either of these curves agrees reasonably with the measurements, with the lower estimate (starting from 250) actually favored.

Concentrate samples 8 and 10 (no concentrate was collected in run 9) show a noticeable rise and fall in concentration level. The rise during run 8 is thought to be due almost certainly to the fact that the reservoir had emptied and no new flow had replenished the flow of product removed. During run 9, new feed was added to the reservoir resulting in dilution of loop fluid. Readings of concentrate conductivity during this period are shown in Figure 6. This figure traces a conductivity rise from the previous level of 1900 or so upward to just over 2300 before the addition of new feed. While the rise in conductivity during the collection of 8C was about 10 percent, it was not the 25 to 28 percent indicated by T.O.C. and NH_3 analysis. Inasmuch as all solutes were affected by the same volumetric dilutions and compressions, and the levels of rejection were not grossly different, one would expect to produce proportional variations of each solute. Using the conductivity as a guide one would predict only about a ten percent rise in loop T.O.C. or NH_3 during run 8.

After the addition of new feed, one expects to see the resulting loop concentration very quickly mix to a new value approaching the "old value" observed before run 8. This value would be expected to be maintained by new feed addition. Unexpectedly, however, the loop conductivity shows evidence that a continuing mixing with low conductivity fluid occurred driving the conductivity to a low value. A similarly low value of both T.O.C. and NH_3 were registered as shown in Figure 5. The concentrate was collected at the end of the run, whereas the product was continuously collected and properly reflects production from a level of about $3/4 \{10C\} + 1/4 \{8C\}$ rather than production from 10C.

Figure 5 also shows results obtained for NH_3 . With feed concentration of 24 ppm initially one would expect only about 53 ppm loop concentration. However, levels generally above this were observed. The possibility that the feed concentration exceeded 24 ppm is therefore considered. Beginning at levels of loop concentration of 60 to 80 ppm one predicts the curves shown in Figure 5 which do not strongly disagree with the data. Use of feed concentration of 28 ppm and initial feed concentration of 60 ppm yields consistently over the concentrating period and agree with the data as well as any curve shown.

No appropriate comparison can be made for the measured values of C.O.D. due to the relatively higher scatter. The data in Table II for samples 1C through 10C have an average value of 586, and the repeatability is not considered good. The high value anticipated for all indices on sample 8 is not indicated by either reading on sample 8. The average value of 586 should be accompanied by a value of T.O.C. of at least 217, which is observed by all data except 10C.

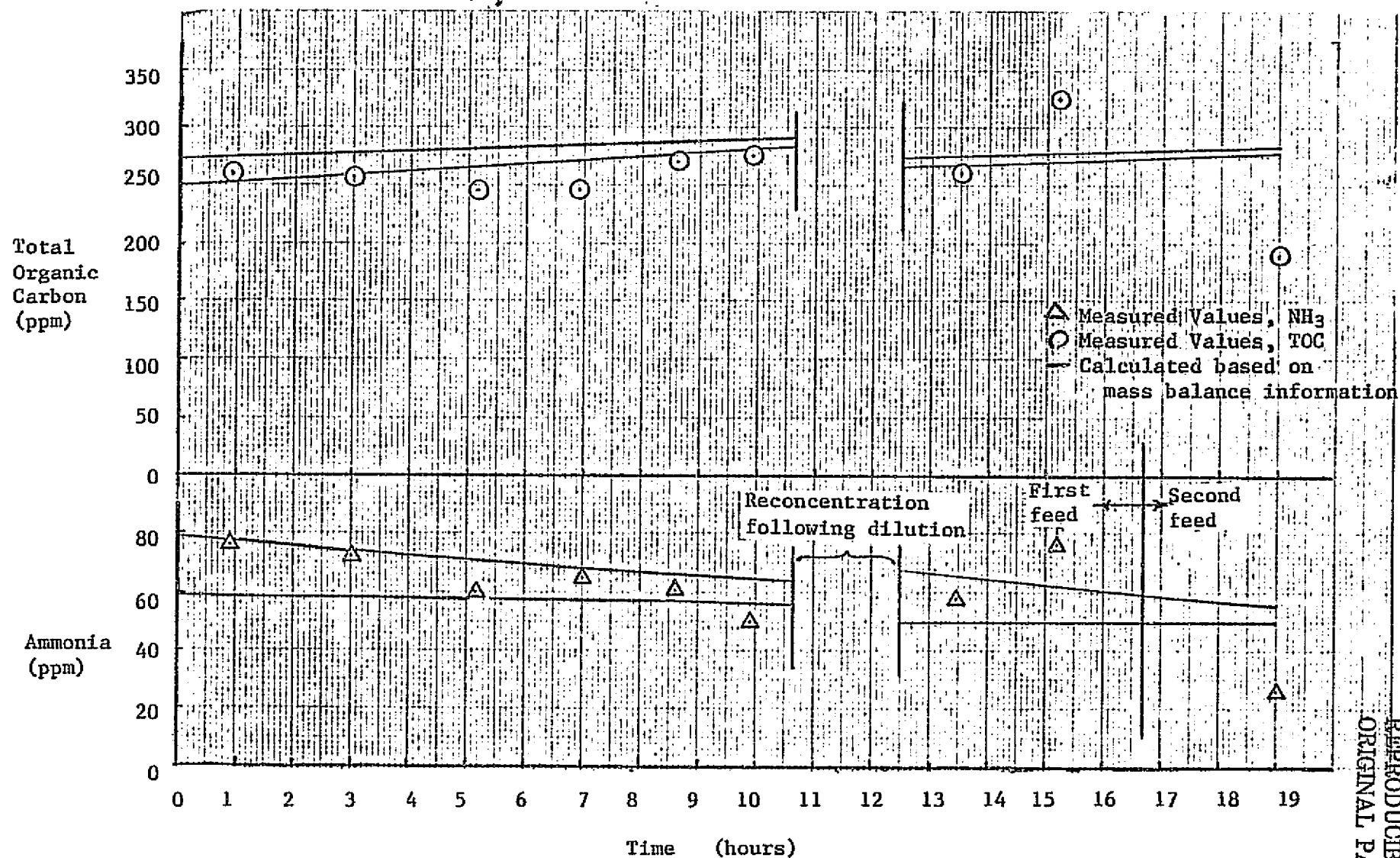


Figure 5. Predicted Concentrations of Loop Solutes

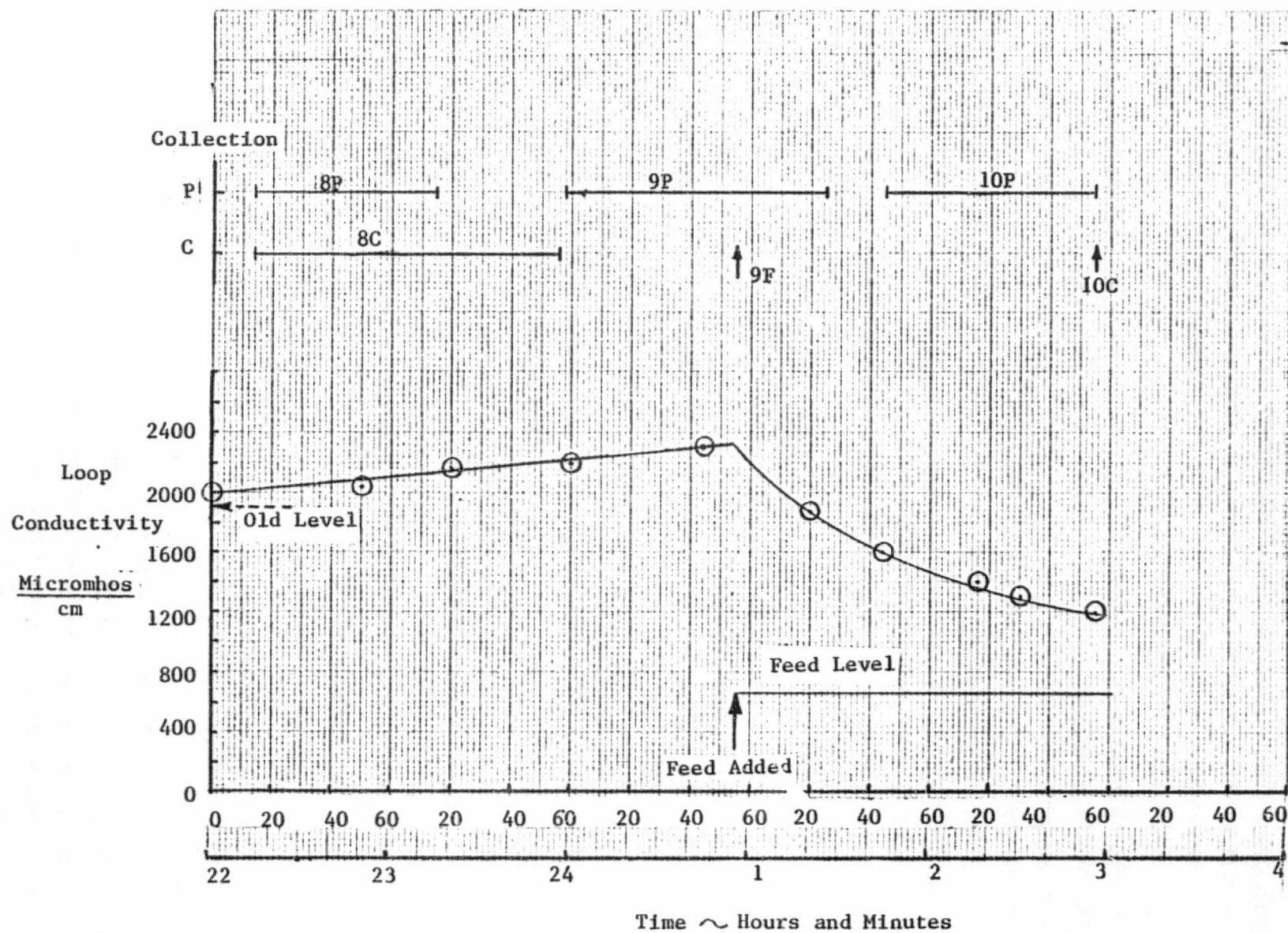


Figure 6. Concentrate Conductivity Readings During Runs 8, 9, and 10.

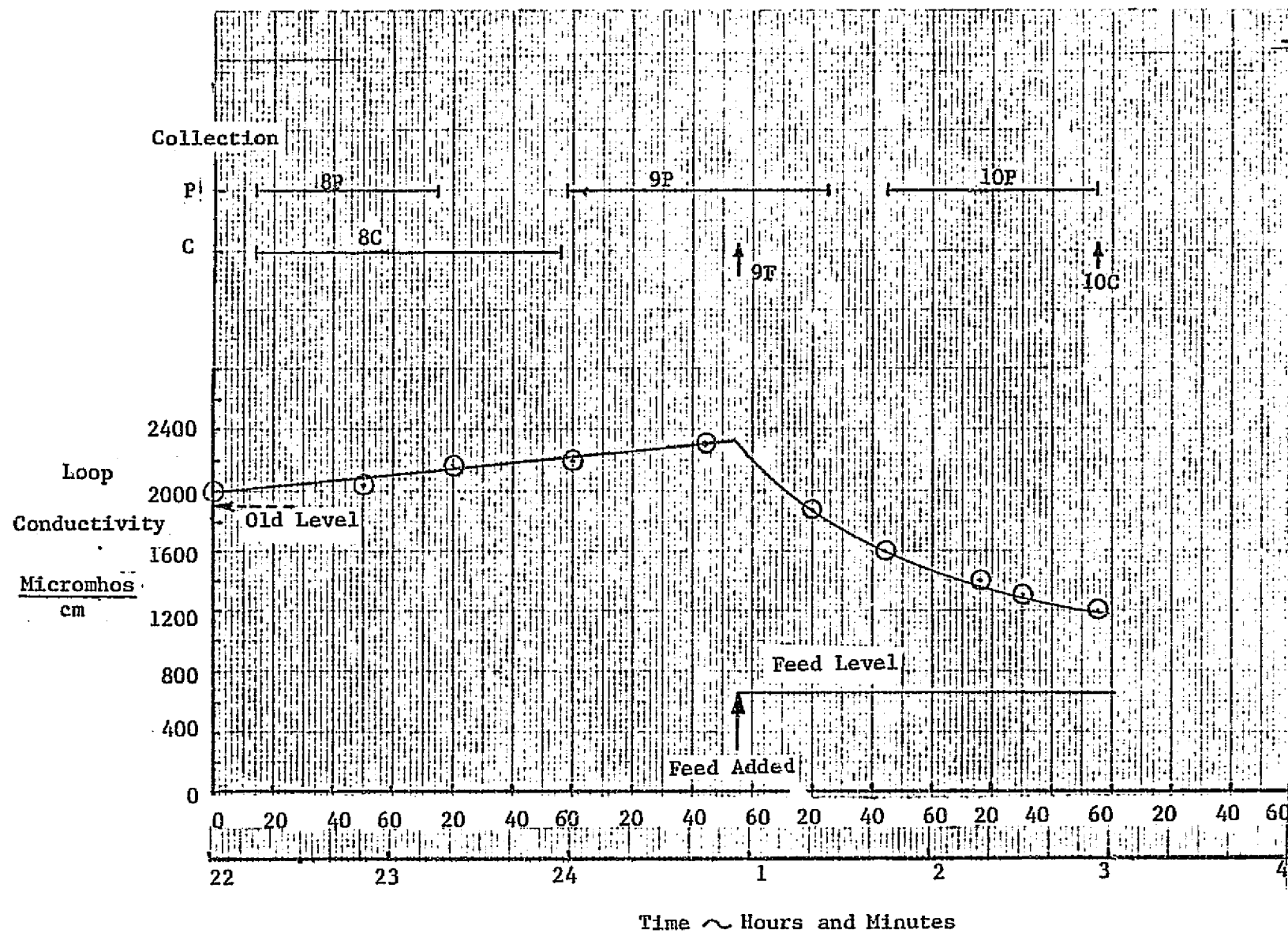


Figure 6. Concentrate Conductivity Readings During Runs 8, 9, and 10.

The concentration scan experiment was performed following the other parametric runs. The first attempt was terminated due to a loss of the pump seal after about 10 hours of running. A new seal was installed and new feedwater was generated after a four day down time. Figure 7 shows the flow rate history and observations of system content. System content was judged by the height of liquid in the feed reservoir. A second feed-water batch was added on the following day with care exerted to insure that the new and old temperatures were equivalent. The integrated flow rate measurements were fitted readily to the reservoir volume observed and allowed extension past the "empty" point to the end of the test, at which time the fluid was drained and measured. In all 9.33 liters of concentrate remained at the end of the test. The data in Figure 7 have been used to determine the recovered fraction R from:

$$R = \frac{\text{liters product produced}}{\text{liters initial volume}} = \frac{\text{initial volume-system content}}{\text{initial volume}}$$

A concentration factor is useful and is defined by

$$\frac{1}{1 - R} = \frac{\text{initial volume}}{\text{system content}}$$

This factor will be used in several of the following graphs. Discrete values are given in Table III for each product sample. Feed samples were collected at the beginning of testing (12C = 12F) and after mixing the second feed with the slightly concentrated earlier feed (denoted 13C). Product sample 13 was not collected at the same time as feed sample 13, but later as shown in Figure 7.

The flow rate history shown in Figure 7 is highly interesting. The membrane is that used for the earlier tests and (referring to Figure 4) had started at product flow about 17 cc/min. During the test, upon the addition of feed (in run 9) the flow declined over about one hour to 9 cc/min. At the initial point in the concentration run the flux had recovered 75 percent toward its original value. Then within 12 hours (no data were taken earlier) the flux had again dropped noticeably. By the end of 36 hours, the flow had risen to a greater rate than that measured at the start of the concentration run. Again, following the addition of new feed, the flow dropped and recovered. The recovery this time was to a level of about 30 cc/min, a value which represents 2/3 of the temperature-corrected flux at formation. Thus, a considerable but incomplete flux recovery had transpired by the end of the concentration test.

Fluid was not withdrawn during the concentration run because it is difficult to account for its withdrawal when calculating the effective recovery; and near the end of the test, a one-liter sample constitutes a significant (5 to 10%) fraction of total fluid. Because of this fact it is necessary to reconstruct the concentration values of solutes in the loop from mass balance information. As shown in Appendix A and elsewhere, the loop concentration (C_c) is related to the feed concentration (C_f) and recovery (R) by

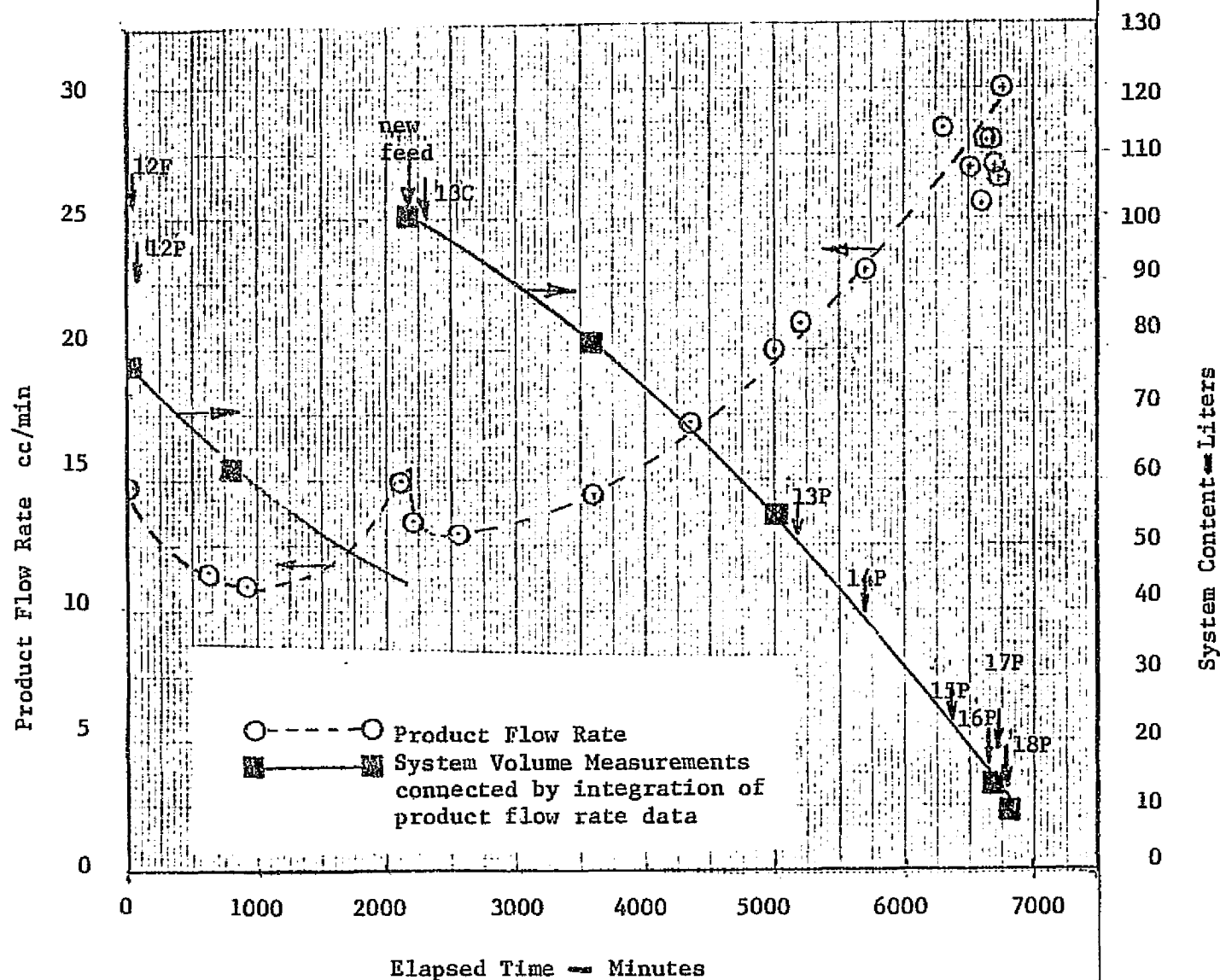


Figure 7 Flow and System Content During Concentration Run

Table III. Concentration Factor for Various Product Samples

<u>Sample Number</u>	$\frac{1}{1 - R}$
12P	1.0
13C	1.32
13P	2.62
14P	3.39
15P	5.83
16P	9.85
17P	11.0
18P	12.3
20C }	14.4
21C }	
22C }	

$$\frac{C_c}{C_f} = \left(\frac{1}{1 - R} \right)^\gamma \quad (1)$$

where γ is the rejection $1 - C_p/C_c$. Such a relation should plot as a straight line on a plot of $\log C_c/C_f$ versus $\log 1/(1 - R)$. Also, at any time, the product must be described according to

$$\frac{C_p}{C_f} = (1 - \gamma) \left(\frac{1}{1 - R} \right)^\gamma \quad (2)$$

Here again $\log (C_p/C_f)$ versus $\log \left(\frac{1}{1 - R} \right)$ is anticipated to be a straight line if γ is constant. The data for T.O.C. are presented in Figure 8 according to these relations. One seeks to determine an average value of γ which causes mutual agreement between the product and feed and the residual concentrate and feed. For T.O.C., the residual concentration is beyond the highest possible value, a condition indicating greater total organic content after the test than before. In Figure 8 two values of feed T.O.C. are employed: the open symbols use the value associated with the higher of the two feed batches, the filled symbols denotes value calculated as the average of two feed batches, judging from sample 13C taken after mixing the second feed batch. The product and feed comparison indicates that a value of 90 or 92 percent approximate the results. These results (92 percent on product data alone and 100 percent on concentrate data alone) do not close the material balance entirely. The feed uncertainty bias can be removed by comparing product samples with only the residue. The maximum value of C_c is that of the residue and occurs at R_{\max} , so

$$\frac{C_{c \max}}{C_f} = \left(\frac{1}{1 - R_{\max}} \right)^\gamma \quad \text{and} \quad (3)$$

$$\frac{C_c}{C_{c \max}} = \left(\frac{1 - R_{\max}}{1 - R} \right)^\gamma \quad (4)$$

The value of product compared to maximum concentrate is then

$$\frac{C_p}{C_{c \max}} = (1 - \gamma) \left(\frac{1 - R_{\max}}{1 - R} \right)^\gamma \quad (5)$$

The relation also plots a straight line in coordinates

$$\log \left(\frac{C_p}{C_{c \max}} \right) \quad \text{vs} \quad \log \left(\frac{1}{1 - R} \right)$$

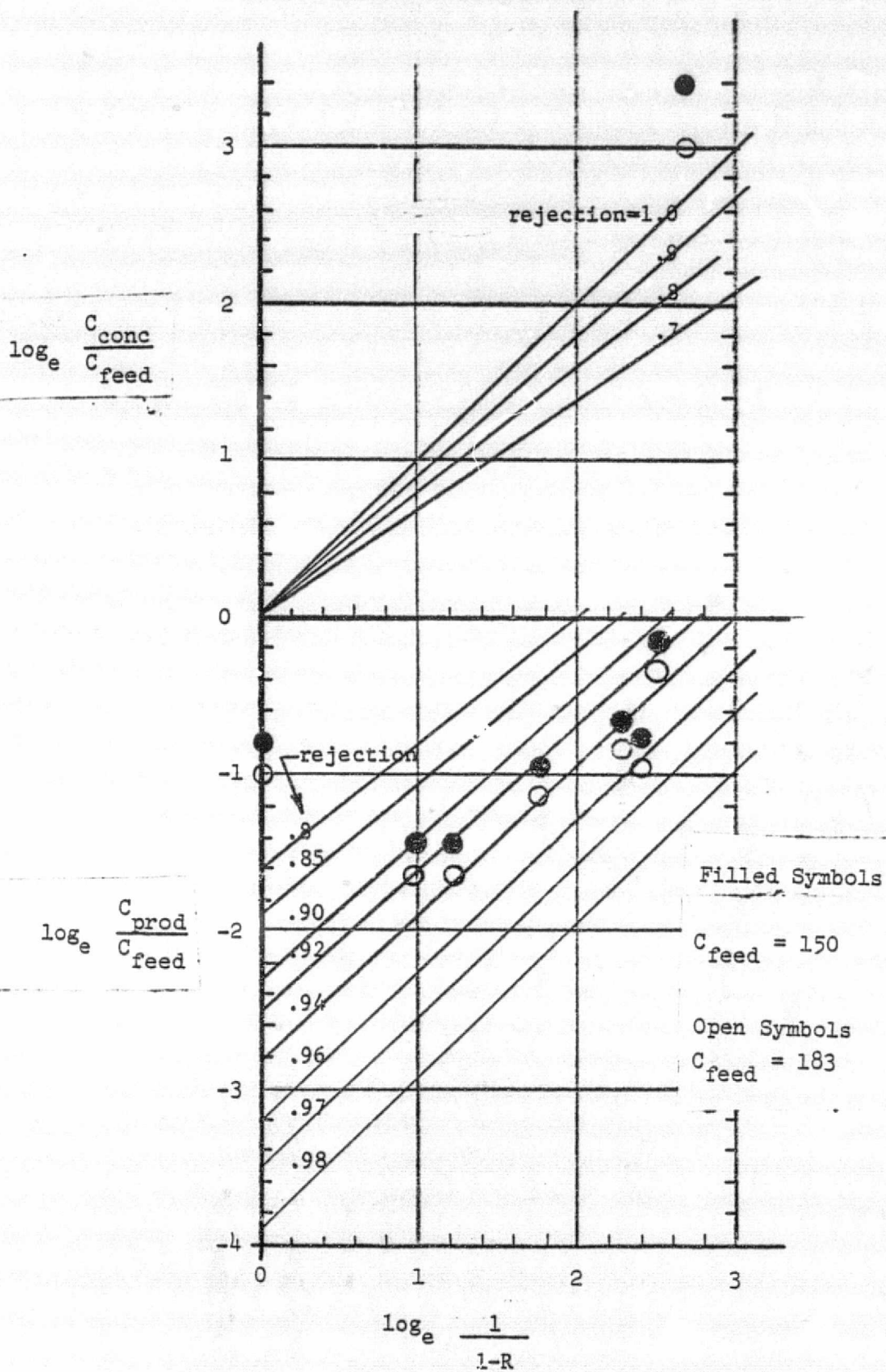


Figure 8 Product Feed and Concentrate Self-Consistency Comparison for Total Organic Carbon

The T.O.C. data are shown in Figure 9 with open symbols for the lower and filled symbols for the higher value of concentrate residue. This approach is felt to be more accurate (assuming equal fidelity of the analysis) for the critical, high-concentration end of the test. The overall indications are that T.O.C. rejections of about 96 percent were achieved.

An identical procedure has been followed for the ammonia data, as shown in Figures 10 and 11. In the case of ammonia, the concentration of residue fluid is lower than would be anticipated based on feed and product data. For urea, only the values of product-to-residual concentration are displayed in Figure 12.

The foregoing procedure has been used to reconstruct a variation of loop concentration which is believed to be basically accurate. Specifically, values of 0.96 and 0.8 and 0.6 have been used for the average rejections of T.O.C., NH_3 , and urea respectively. The concentration which leads to the measured residue values is used; i.e. the concentrations are computed from equation 4. This leads to concentration estimates which are believed to be more reliable at the higher concentration levels, since the feed concentration is ignored in favor of the residue concentration.

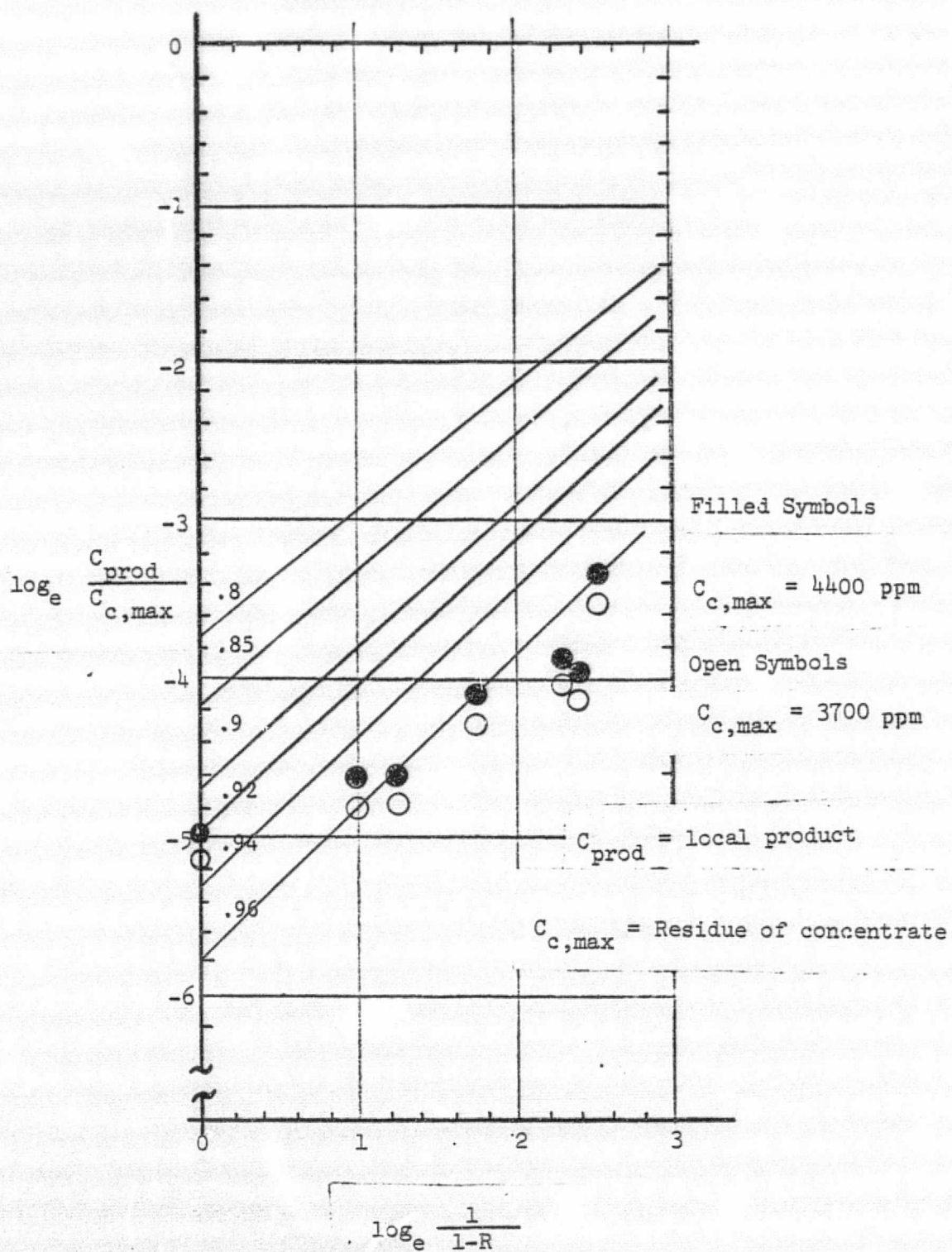


Figure 9 Product and Residue Self-Consistency Comparison for Total Organic Carbon

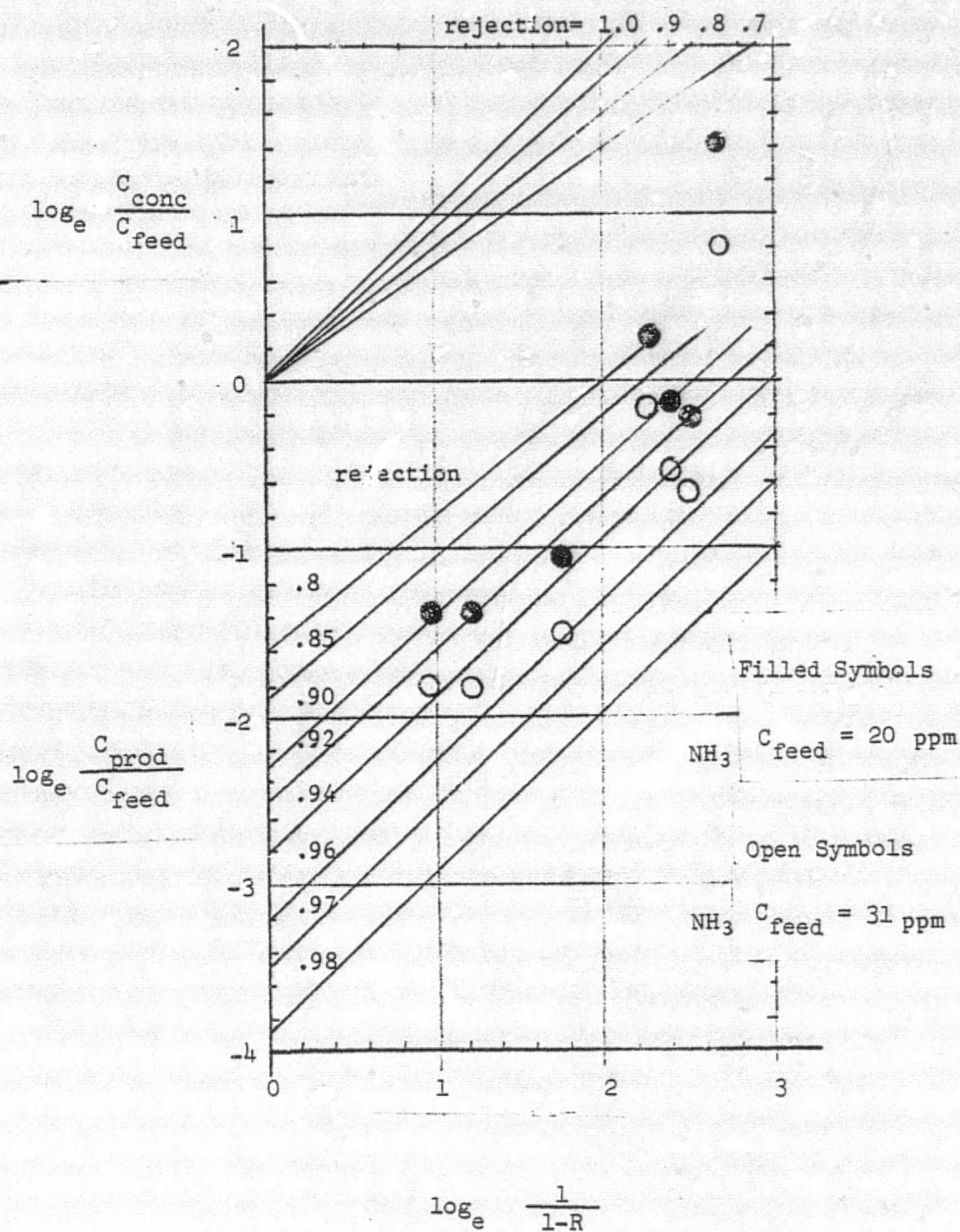


Figure 10 Product, Feed and Concentrate Self-Consistency Comparison for Ammonia

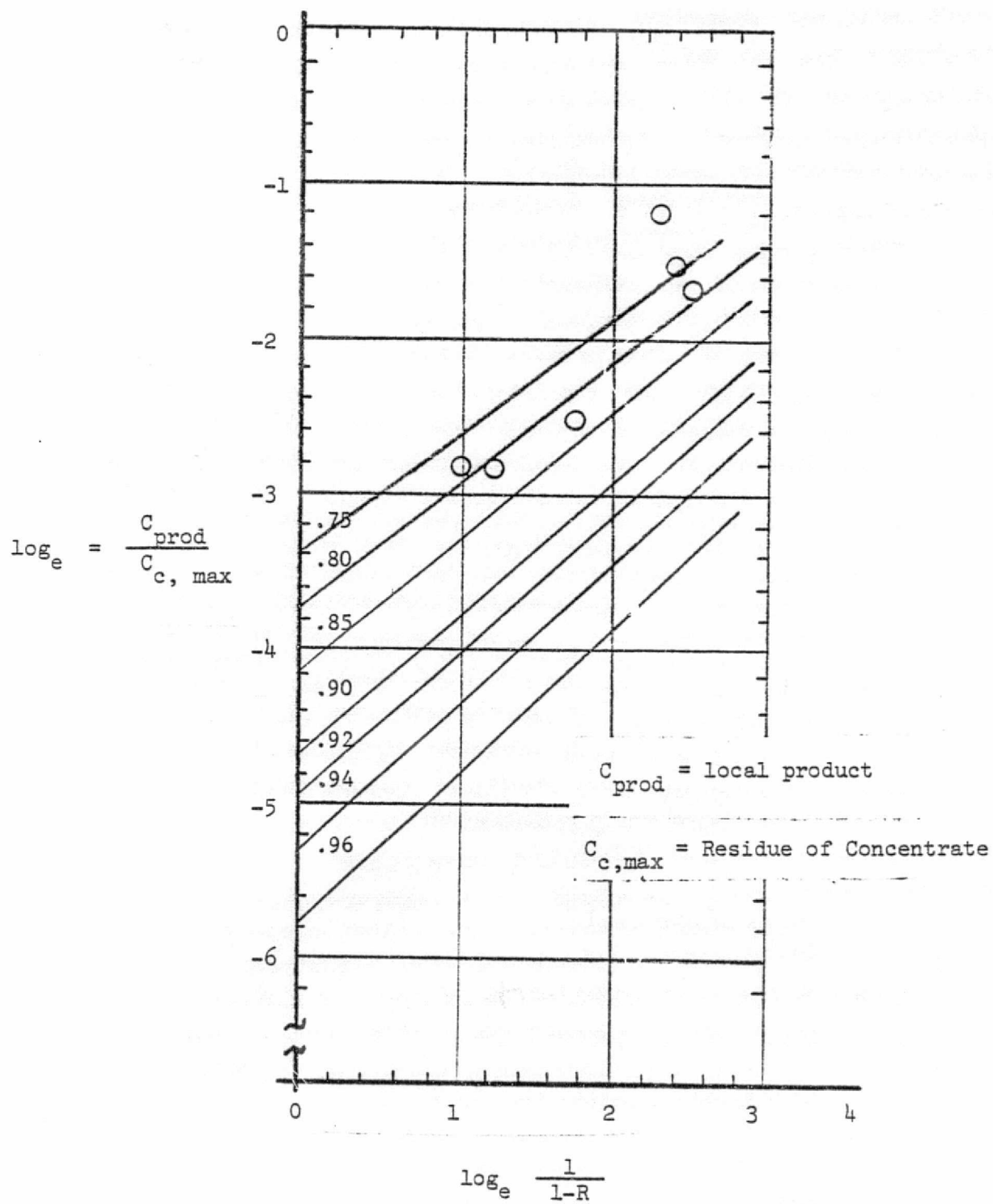


Figure 11 Product and Residue Self Consistency Comparison for Ammonia

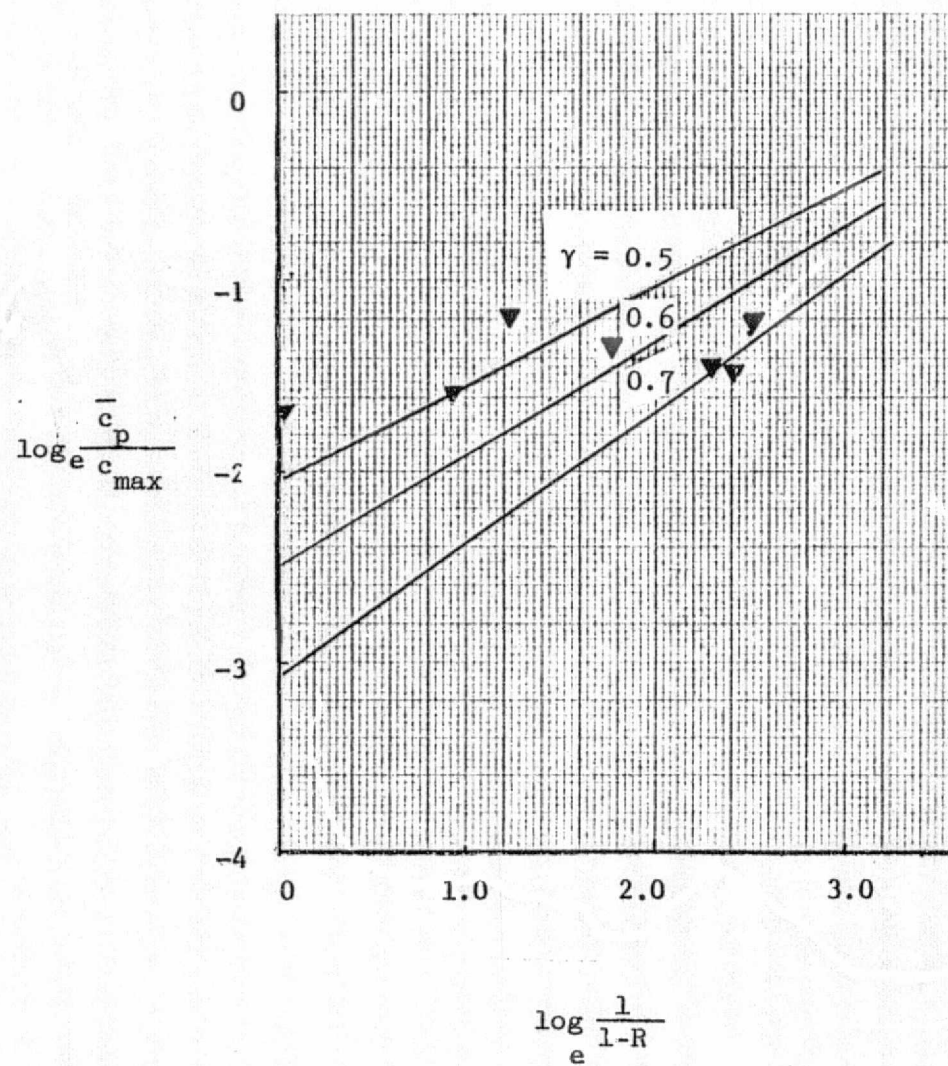


Figure 12 Product and Residue Self Consistency Comparison for Urea

6.2 Results

The parametric tests were carried out in two parts. During a 19 hour period terminating at 0300 hours on July 3, the systematic variations of pressure, temperature, and circulation velocity were accomplished. After some system repairs, the concentration scan was carried out on July 8 through July 13.

The range of variations were selected, consistent with system capabilities, to cover the expected range of interest for the design of a wash-water recovery system. For example, temperature was not varied below 348°K, since it was expected that considerations of sterilization precluded system designs for lower values. Preliminary analyses for optimum system design indicated high pressure and low velocity. Thus the range of variation from the standard was weighted accordingly. Based on previous observations with shower water and general experience with dynamic membranes, the standard conditions were: $V = 8.2 \text{ M/sec}$; $T = 348^\circ\text{K}$; $P = 6.55 \times 10^6 \text{ N/M}^2$ (950 psig) and $C = 2.5 \times \text{feed concentration}$. Only one parameter was varied at a time from these conditions.

Of course, a perhaps significant variable about which little is known is time. In each parametric scan the tests were started and concluded at the reference conditions. No significant variations were noted that are attributed to time over the three or four hours elapsed during each parametric scan. In Figure 4, a presentation of the major event chronology, the sequence of variations during the parametric tests of pressure, temperature, and velocity is indicated. Also noted are the times during which samples of the product and concentrate were collected. These samples are the basis for the determination of membrane performance, with respect to the rejection of certain key solutes in the shower water. In several figures, the results of the parametric scans are presented in terms of the observed rejections of total organic carbon (T.O.C.), conductivity, ammonia, chemical oxygen demand (C.O.D.), and urea.

6.2.1 Pressure

In Figure 13, the observed rejections and product flux are plotted against pressure. During this scan pressure was varied from $5.25 \times 10^6 \text{ N/M}^2$ (750 psig) to $7.1 \times 10^6 \text{ N/M}^2$ (1040 psig). To indicate the probable trend to lower pressure, data from hyperfiltration of industrial wastewater are shown. The observed rejections are apparently constant over the range of pressure investigated. However, the rejection is expected (2) to increase with pressure approaching an asymptotic value. Consequently, it is probable that performance slightly above the rejection levels indicated can be achieved.

The flux is indicated to be a linear function of pressure going to zero at zero pressure. The molality of solutes is quite low in the shower water; hence no significant shift in a zero intercept due to osmotic pressure is expected. The results with the industrial wastewater also indicate a linear relationship with zero intercept. The indicated levels of observed rejection for the several parameters are:

- (1) 96% for T.O.C.
- (2) 91% for conductivity
- (3) 87% for ammonia
- (4) 84% for C.O.D.
- (5) 76% for urea

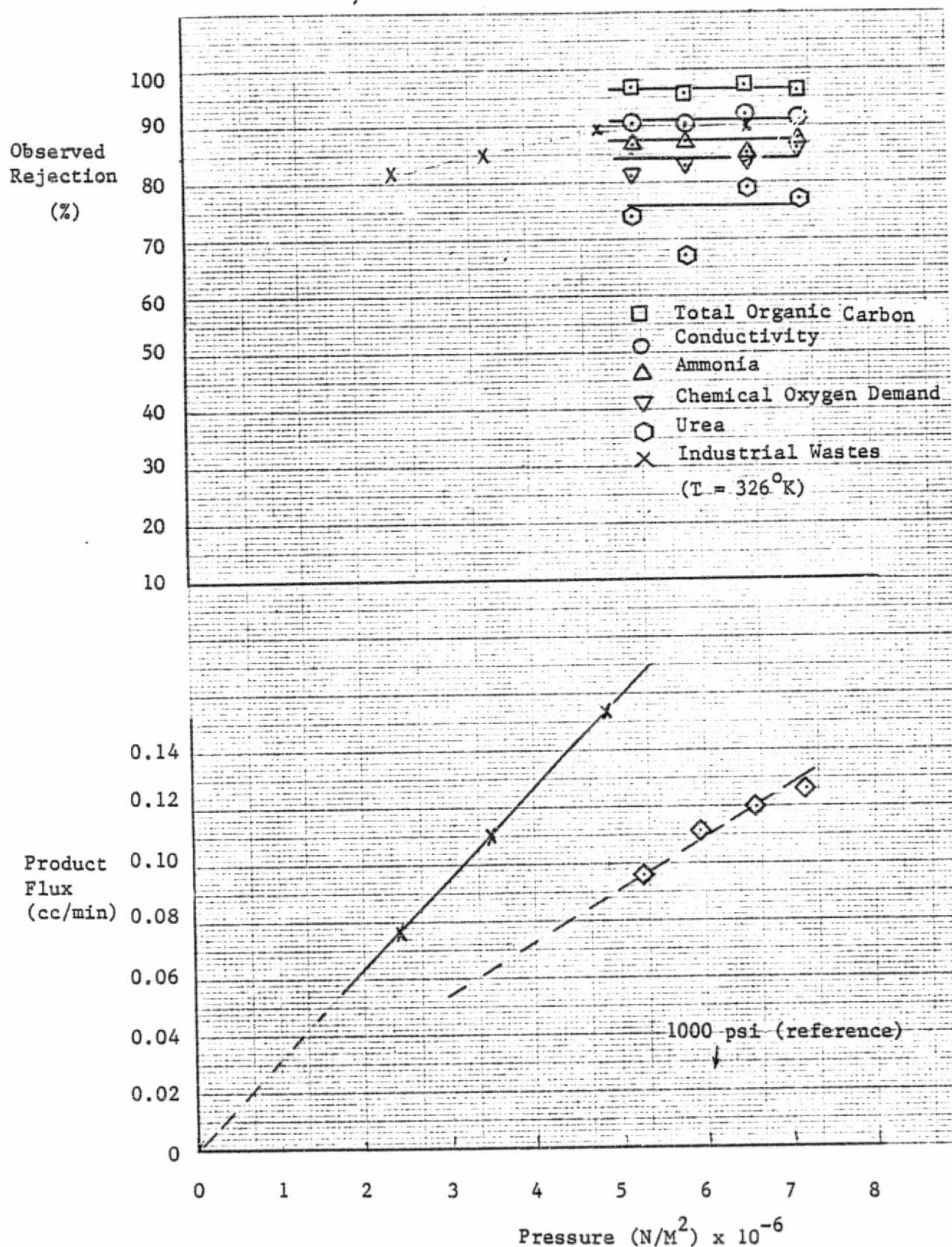


Figure 13. Performance Variation with Pressure
($U = 8.2 \text{ M/s}$, $T = 348^\circ\text{K}$, $C = 2.5 \times \text{feed}$)

6.2.2 Velocity

In Figure 14, the observed rejections and product flux are plotted against velocity. During this scan velocity was varied from 8.2 M/S to 1.7 M/S. Two types of velocity effects are important in hyperfiltration. The short term effect, concentration polarization, (a mass transfer phenomenon) is indicated by a decreased observed rejection. Longer term effects due to surface "fouling" or "scale" build-up are expected to be related to circulation velocity as well as temperature. Unfortunately, several unscheduled events occurred that cloud the interpretation of the observed results.

At the start of the velocity scan, it was necessary to go through a re-concentration period due to dilution of the loop feed resulting from a change of flowmeters. Some 5.5 hours later, in the middle of the test at 2.5 M/S, the system volume had to be replenished with a second batch of shower water (see Figure 4). The pH of the new material was 4.7 compared to the pH = 7 for the original. The indicated time dependence of flux makes the interpretation of the results from the tests at 2.5 M/S and 1.7 M/S uncertain.

For the conditions of these tests little concentration polarization effect was expected. All the observed rejections confirm the lack of dependence upon velocity, certainly in the range of 2.5 M/S. The indicated much lower rejections for ammonia and urea are of particular concern since these solutes are the limiting factors for product water reuse. It is felt that the phenomena indicated at these lower velocities are more related to the addition of new feed than to low velocity.

Unfortunately, there is no completely satisfactory explanation for the lower urea and ammonia rejection. Since the minimum permissible velocity is very critical to module and system design, further explanation of the low velocity results is essential. Bearing in mind that long term velocity effects have not been investigated either, it seems reasonable to conclude that the present results confirm expected short term velocity effects on observed rejections.

6.2.3 Temperature

In Figure 15, the observed rejections and product flux are plotted against temperature. During this scan, temperature was varied from 76°C to 93°C. To indicate expected trends to lower temperatures, data from hyperfiltration of industrial wastewater is shown. The observed rejections clearly indicate a trend to decrease with increasing temperature. This is a result of the coupling of the solute flux to the water flux which is shown to increase markedly with temperature.

The data are connected by a dashed line in Figure 15. To yield further insight into the mechanism by which the water flux increases, the data are re-plotted in Figure 16 with the logarithm of flux against the reciprocal of the absolute temperature. The results in Figure 16 are suggested for predictive interpretations. Other data indicate this trend continues to at least 25°C.

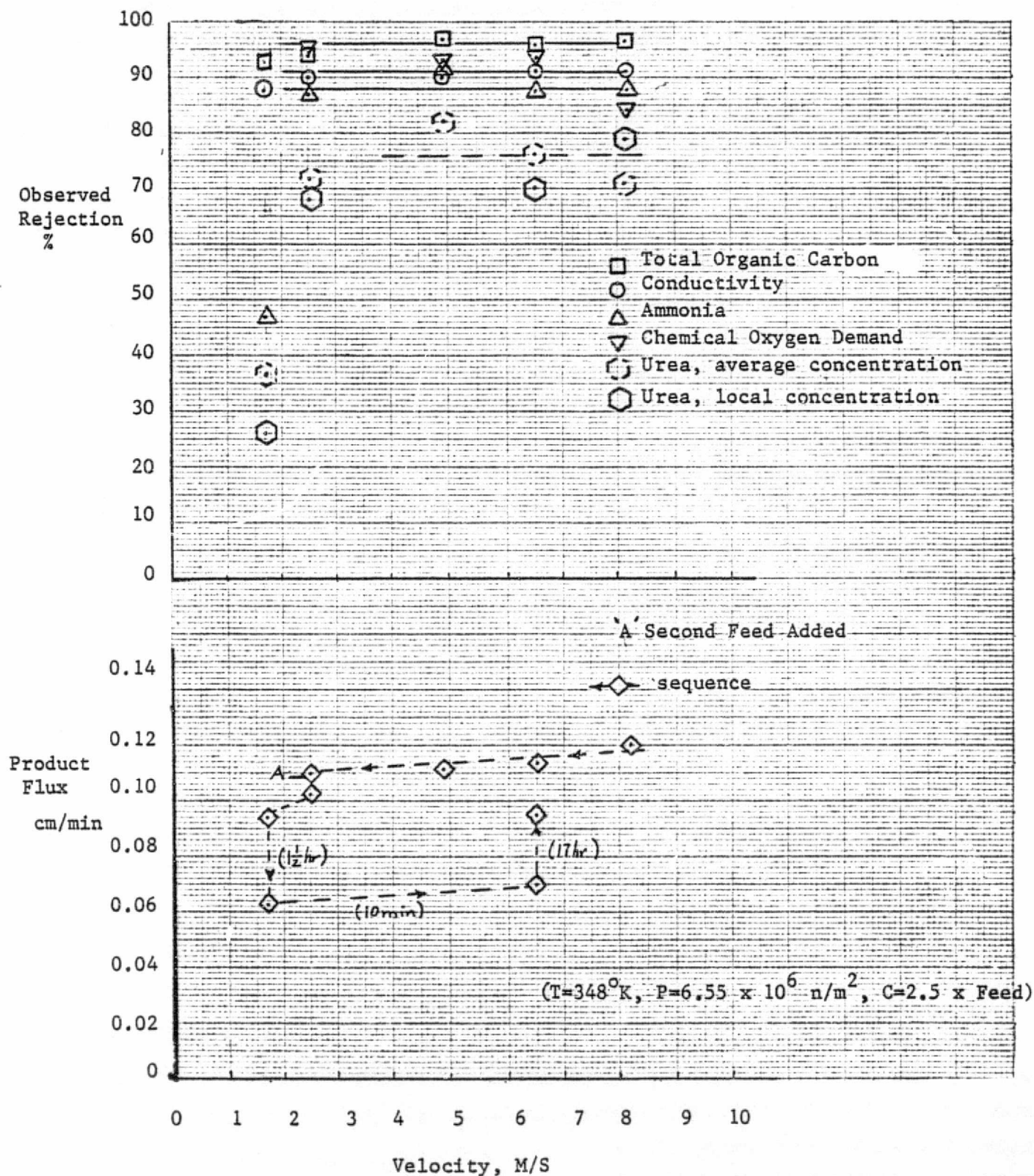


Figure 14 . Performance Variation with Velocity

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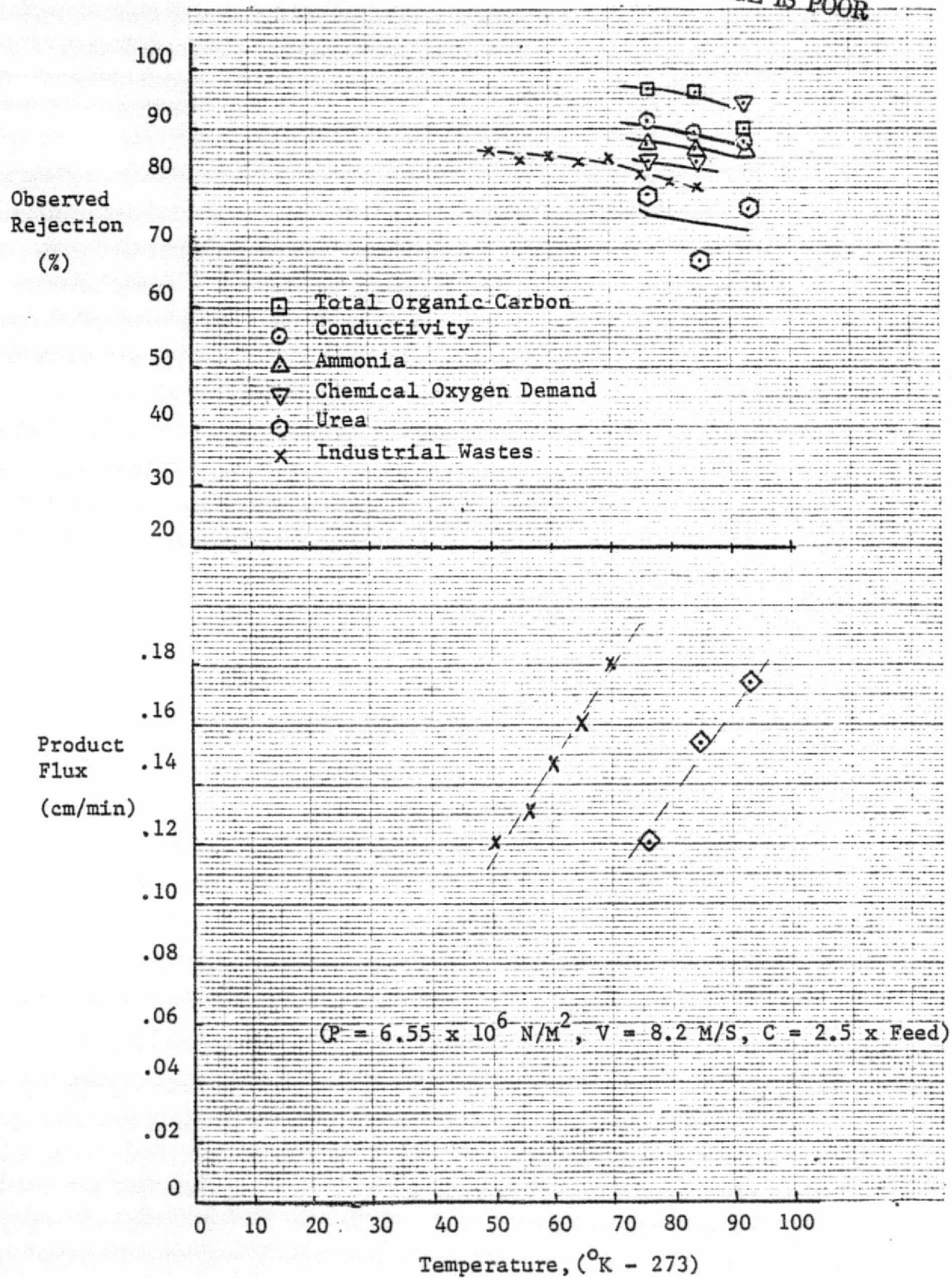


Figure 15. Performance Variation with Temperature

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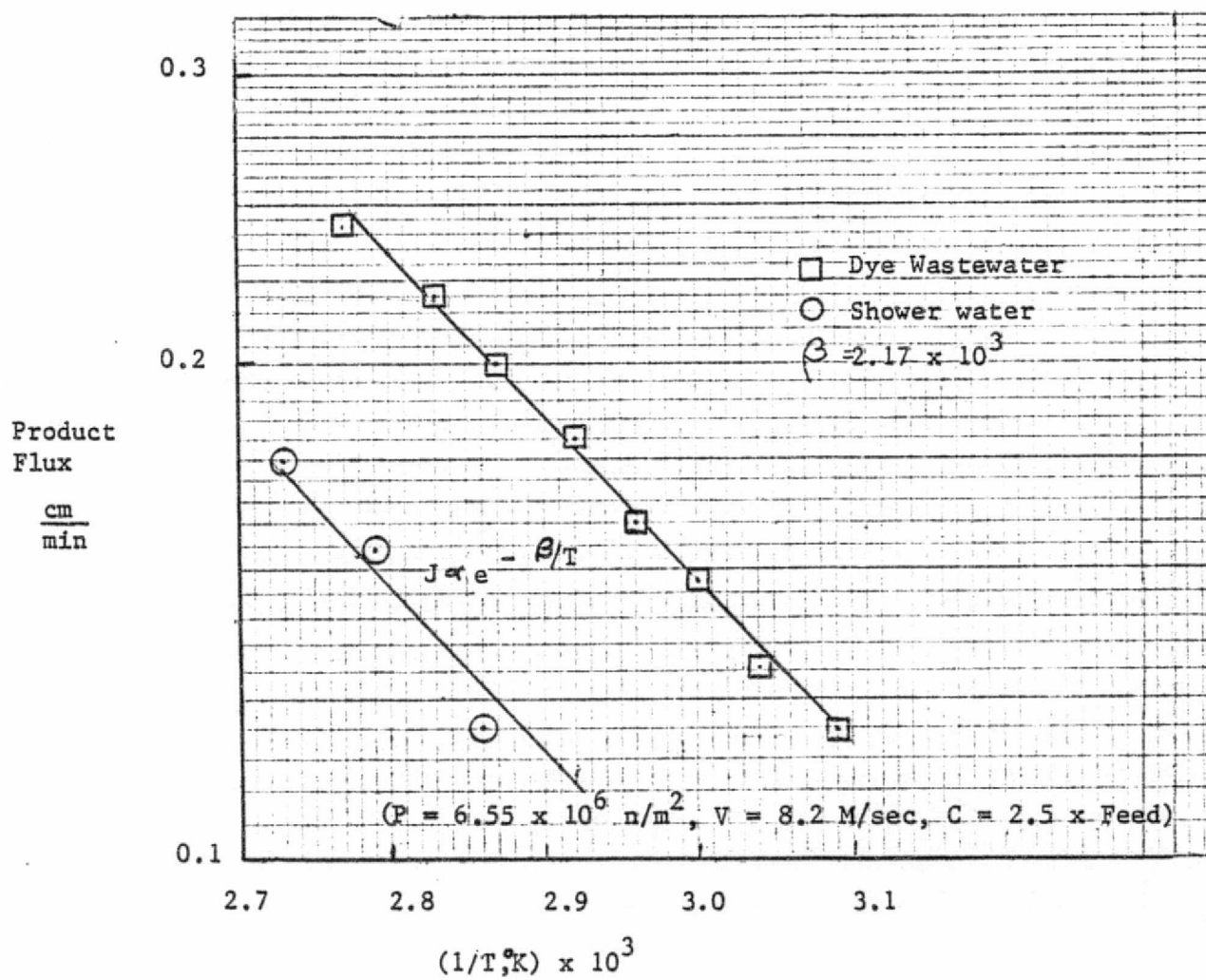


Figure 16 . Variation of Product Flux
with Temperature

The outstanding effect of temperature is marked increase of product flux with temperature elevation. This is accompanied, however, by a decrease in rejection of solutes in the shower water.

6.2.4 Concentration

Following a total loss of shower water because of a failure in the pump seal, the concentration scan was carried out during a 116 hour period on July 8 through July 13. While the significance, if any, is not known, it is noted that the membrane was isolated in shower water during the 4 days that the pump repair was effected.

In Figure 17, the variation of the concentration of T.O.C. and ammonia in the product water is shown as the mixed product concentration versus the fraction of feed collected. The variation in the product flow rate is used to determine the concentration of the accumulated mixed product. The end of the test was determined by the minimum system volume for stable pump operation, not by any item related to processing difficulties.

The mixed product concentrations for these important solutes are 37, 6.5, and 50 for T.O.C., NH_3 , and urea, respectively. Since NH_3 must be held to within 1 ppm, additional processing will be required. In one pass of 93 percent recovery, the NH_3 level was reduced from 24 to 6.5. An additional reprocessing will result in a concentration of $6.5 \times 6.5/24$ or 1.76. Thus a two stage process will nearly result in acceptable water quality.

In Figure 18, the rejection of the three solutions, T.O.C., NH_3 , and urea are shown against the recovery factor, i.e. the concentration factor based on volume of collected product. The flow rate history of this scan during its earliest stages has been discussed and shown in Figure 7. The influence of fresh feed on the membrane is not well understood, but certainly seems significant. Other experiences with industrial wastes have also indicated a period of accommodation between feed and membrane. This accommodation as regards flux and salt rejection has normally proven to be reversible.

The influence of concentration per se on the rejection of solutes was not found to be significant for T.O.C. There seems to be a significant reduction in ammonia rejection for high concentration factors. The general data of the parametric runs had resulted in NH_3 rejection about 0.88, while the results at high concentration tend toward 0.8.

Urea rejections of perhaps 0.75 were indicated during the parametric data runs, while the low concentration portion indicates a substantially lower value. These low concentration data are not highly accurate as the reconstruction of concentrate level from a mass balance using residual analysis can lead to errors. However, these errors decrease as the higher concentration is approached. The level of urea rejection may well be about 0.70, but an average value of 0.6 is claimed. Either value should result in acceptable separation if multistage filtration is adopted.

6.3 Conclusions with Respect to End Item Design

Ammonia concentration appears to be the primary design item, having an expected feed concentration of 20 to 30 ppm and a product target of 1 ppm.

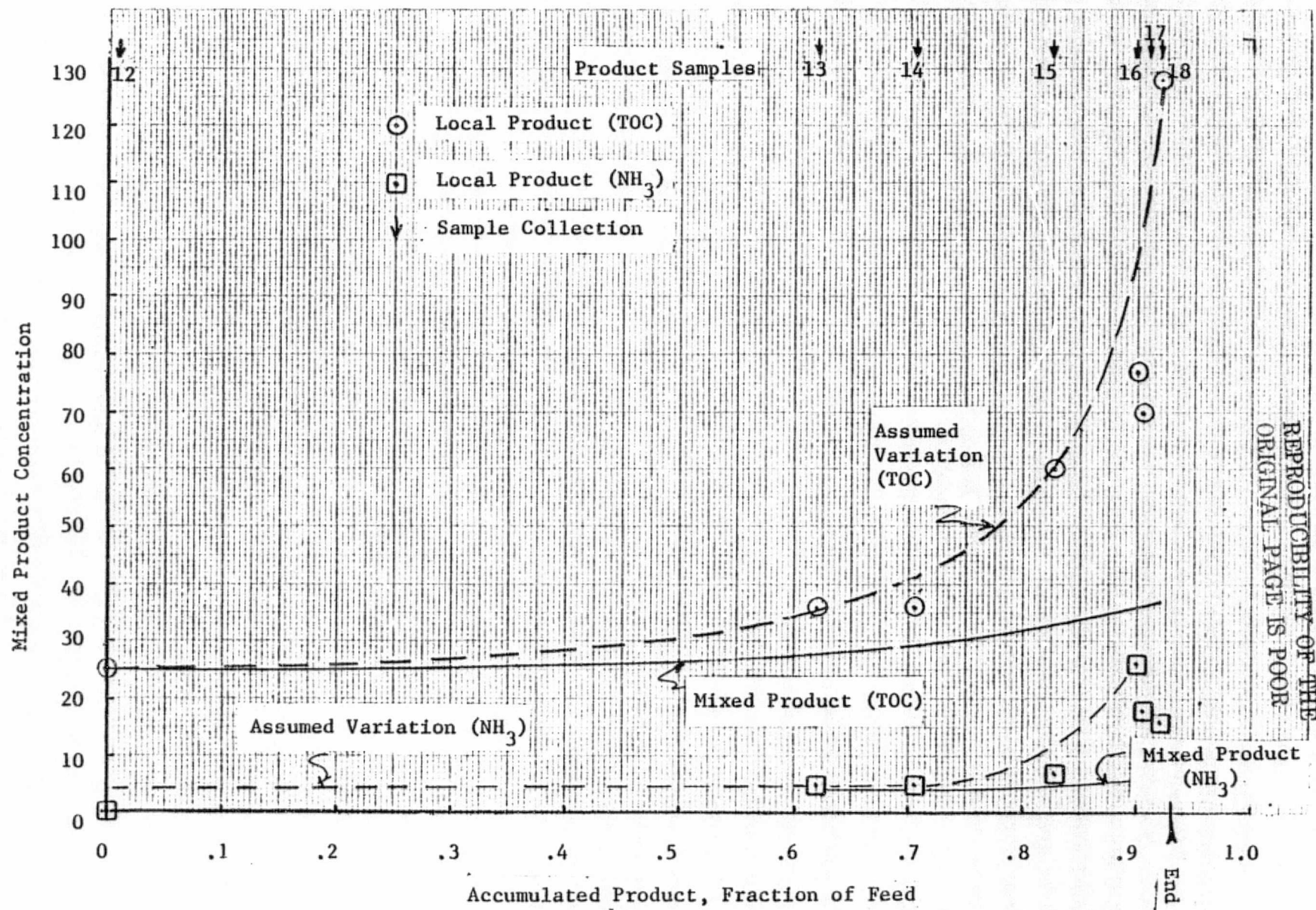


Figure 17 . Calculation of Product Water Quality versus Feed Recovery

$$(P = 6.6 \times 10^6 \text{ n/m}^2, V = 3 \text{ to } 7 \text{ M/sec}, T = 75^\circ\text{C})$$

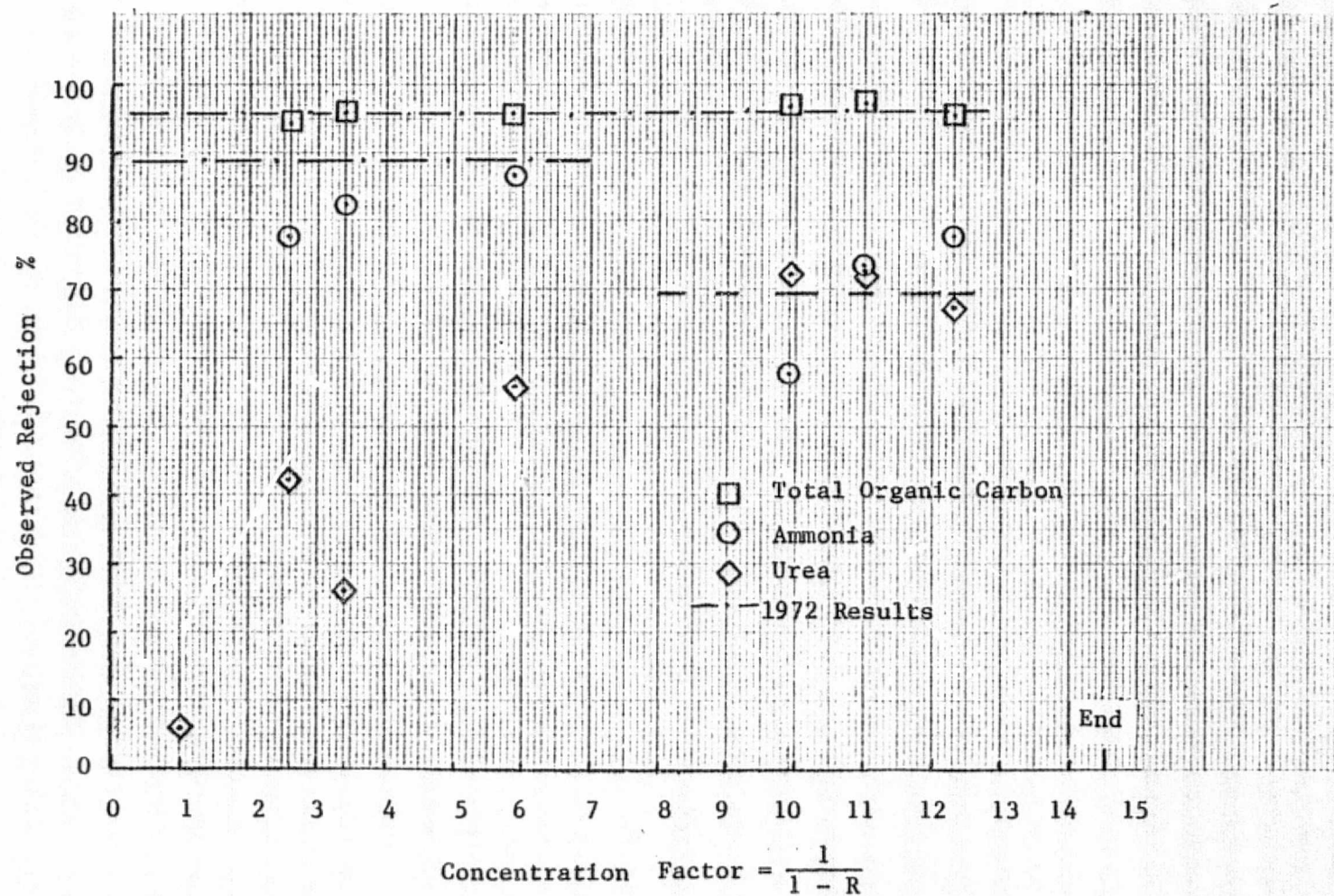


Figure 18 . Observed Rejections During Concentration Scan

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While it is possible to consider controlling the breakdown of urea to ammonia, thus reducing the feed concentration, the following assumes direct filtration.

Figure 19 shows the schematic diagram of a system which, according to the data reported herein, will meet the accepted potability requirement. The module is a once-through type design which produces 93 percent product water and 7 percent reject. The product water is tested on line and compared to the allowable value. If the concentration is unacceptably high, the product is mixed with the feed batch, thus lowering its concentration. When the product issues at an acceptable level, it is allowed to pass into the water storage reservoir. The single stage recovery (93 percent) is not constrained; however, its value is a factor in the overall recovery and the required pump flow rates. On the average, almost three feed volumes of fluid must be processed before acceptable product has been completely produced. Each time a feed volume passes, 7 percent is converted to residue. Therefore about 21 percent of the original feed would become residue, or the system recovery would be 79 percent. It is emphasized that this is a workable example which does not represent any attempt to achieve an optimum recovery. When the ammonia content has been reduced to 1 ppm, the organic carbon will be reduced to about 2 ppm, the urea to about 17 ppm, and most other salts reduced to threshold-of-measurement values.

The data obtained herein are for tubular flow in a 2 mm diameter channel. This channel, with a flow rate of 0.00531 l/sec has a velocity of 1.64 m/sec. Assuming this flow is the exit flow of a 93 percent recovery module, the entering flow to the module is .07582 liters per second. At this flow, and a rise of 130 atmospheres in the pump, one calculates the fluid power to be $1.3 \times 10^7 \text{ N/M}^2 \times 7.58 \times 10^{-5} \text{ M}^3/\text{sec} = 985 \text{ NM/sec} = 985 \text{ watts}$. This rather substantial power requirement may be decreased through development of a smaller diameter flow channel or operation of the membrane at velocities less than 1.64 m/sec. For example, operation at 1 m/sec in a channel 1.5 mm in diameter would reduce the pump power requirement to 340 watts. On the other hand, an increase in the recovery above 93 percent will increase the pump power.

The average flow produced, per tube, in the test reported herein was about 0.002 liters/minute. To produce .07 lit/sec of fluid requires 2100 tubes of this size. Packed in a close hexagonal array, at spacing of 5 mm, this number of tubes would occupy a cylinder 18.3 cm diameter, 35 cm long. This estimate is both conservative and non-conservative, in that the product flow rates should be higher than estimated and in that achievement of a close-packed hexagonal array represents a development problem.

The power required for such a system will depend strongly upon the low velocity which can be tolerated. The velocity enters strongly into the membrane pressure drop; which, at a 2 M/sec is roughly equal to the pressurization itself. Using expected high efficiency components will allow processing under 20 watt hours per kg (9.1 watt hours/lb).

6.4 Experience with Washwater Preparation

The following table relates the Clemson experience in washwater production. All washwater was produced according to Reference 3.

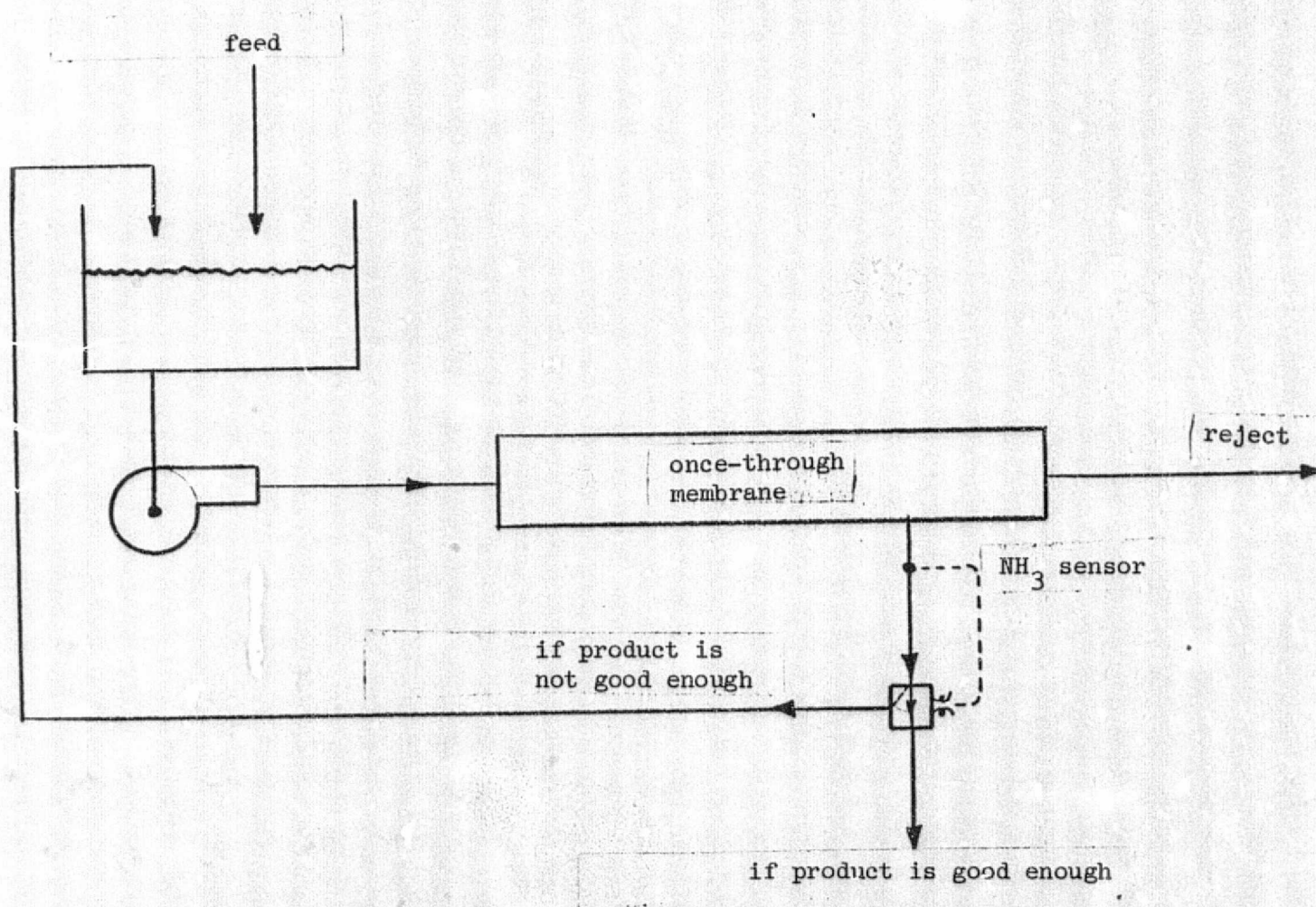


Figure 19 Arrangement of Projected System Used for Estimation

Batch Number	Date Fluid Added	pH	Conductivity (micromhos per cm)	Sample Number	Remarks
1	6-4-75	5.4	670		Poor sample due to lack of soap.
2	7-1-74		530		When generated before adding to pump reservoir.
2	7-1-74	7.4	1000	1F	When added to tank.
3	7-2-74	4.7	660	9F	Before neutralization.
3	7-2-74	7.3	920		After addition of .002 moles NaOH per liter.
4	7-8-74	5.0	535	12F	Before adjustment.
4		6.1	- 640		After addition of 20 g active ingredient of olive leaf in about 70 liters of washwater.
5	7-9-74	6.3			Before standard washwater supplement addition.
5		4.3			After supplement addition.
5		6.0	650	*13C	After addition of 13 g olive leaf in about 70 liters of washwater.

*13C is that produced by slightly concentrated batch 4 plus batch 5.

The first washwater produced was deficient in soap content due to reading the prescription as "grams of soap" rather than "grams of active ingredient of soap". The Olive leaf soap is nominally 20 percent active ingredient resulting in about 20 percent of the prescribed soap amount. The acidity of the solution was counter to expectations and was attributed to the lack of soap when the error was discovered. The next batch of shower water was stored in a closed barrel for several days before addition to the test loop. At generation the pH was not recorded but conductivity definitely increased during storage.

The third batch of shower water was checked just before delivery to the feed reservoir and was strongly acid. The reasons were unknown but the relatively strong variation in water was of concern because of the expected effect on membrane rejection, which could and did confuse the effect of the other parameters. After the immediate test conditions were satisfied, the acid condition was changed by adding NaOH. This action was taken considering several factors.

- (1) It was not considered normal for washwater to have pH below 6.
- (2) While some variations are expected the effect of pH on salt conductivity rejection add an unwanted complication.
- (3) For the sake of greater uniformity, neutralization was considered beneficial.
- (4) The ion rejection performance of the dual layer membrane is better at neutral or slightly alkaline feed conditions so that even if the feed were acid, addition of base might occur.
- (5) A survey of shower takers indicated difficulty in using as much as the prescribed soap amounts. Hence the actual soap content (a basic solution) may still have been deficient.
- (6) Later additions of base should be done with soap rather than with NaOH.

The next batch of shower water was carefully noted to be acidic though perhaps half that of the preceding batch. Estimating that perhaps only half of the expected soap had been used by the bathers, an equal amount was added, then doubled to ultimately yield a pH of about 6.1. The pH of the shower additive used to supplement the test subject's secretions is dictated by the lactic acid component. Shower additive and soap alone added in the prescribed proportions produced a solution having low pH (below 5). This leads us to believe that all wash water produced according to the formula would be acid — contrary to expectations for "natural" washwater.

Further observations were made concerning the generation of washwater. The source tapwater is acid in our laboratory and after filtration through a U.O.P. commercial reverse osmosis unit has a pH of about 6.0 though low in conductivity (below 10 micromhos/cm). After showering and laundering of clothes the pH was 6.3. Upon addition of the shower additive the pH was 4.3. About 0.18 g of active olive leaf ingredient per liter of washwater was required to produce pH = 6.

The concern over feed pH centers in the desire for consistent results which, as nearly as possible, represent the intended application. The rejection of NaCl in dynamic membranes is well known to be highly sensitive to pH in the range below pH = 8. In fact, it is not unusual to observe a 10 percentage point rejection decline from pH = 7 to pH = 6. Whether the acidity index has a profound effect on the rejection of other solutes was not, and is not, known. The reported performance variations near low velocity happened to coincide with the insertion of new feed which lowered the pH by a unit. It is strongly suspected that the pH decrease may have had a larger influence than the velocity in producing the lower values of rejection observed. However, because the effects are inseparable in the data acquired, no certain conclusion can be drawn. Further concern exists in that future testing of pH sensitive membranes conducted on the analog shower water may not represent the intended application. The evidence already presented leads to the conclusion that acid washwater will result from application of the standard procedure.

All reports of prototype washwater indicated that its pH should be neutral to slightly basic. These data suggest the review of the analog washwater generation procedure, particularly with respect to the additive solution composition.

6.5 Experience with Mechanical Design

Membrane mechanical details are considered to be of secondary interest. However, the following discussion is intended to illuminate the experience obtained during the present effort.

Normally the concentrate flow (pressurized) is separated from the product flow by the membrane on a tubular support. The tube serves to afford the membrane structural support, while exerting a minimum impedance to the product flow. To allow structural support it has been determined by experience that the support must be characterized by a small pore size. On supports having a naturally high (above $\sim 1\mu\text{m}$) pore size, it is necessary to first deposit a filter aid upon which the membrane may be formed. The effect of the type of material comprising the support is not known.

Membranes have been formed on the outside and the inside of tubular supports, with product recovery respectively inside and outside the tube. The outside pressurization clearly make use of the advantage of loading ceramic tubes in compression. However, the uniformity and magnitude of important fluid mechanical properties are less predictable. For example, the shear stress (and hence mass transfer rate) on the central tubes is expected to be less by an undetermined amount than the shear stress computed on an average velocity basis. In the reverse osmosis module, as in heat exchangers, the performance is increased by achieving (or forcing) flow uniformity. Similarly the data in uniform flow are not masked by effects of averaging over a range of velocities.

From the aforementioned motivation it was desired to employ several tubes in a parallel flow arrangement. The Selas ceramic tubes had been found to be relatively strong in tension and had pore properties which allowed the deposition of membranes without the use of filter aids. Two types of arrangements were anticipated. One used eighteen single channel tubes in a parallel flow arrangement, while the other used six tubes, each having seven 2 mm diameter channels, in a similar arrangement. Care was taken that misalignment of the tubes and tube sheets sufficient to load any tube in bending was not possible.

On several different occasions, we ruptured tube supports. No particularly extensive investigations were conducted to determine the cause, except to allow reasonable confidence that the ruptures were not caused or aided by external structural loading. Having eliminated design innovation as an immediate solution to the problem, we employed a single, seven channel tube to perform the testing. The tube was mounted essentially as shown in Figure 3, page 13. In this configuration we burst several tubes, but were able to operate with a reasonably high success ratio.

The conclusion made concerning both multiple tube bundles is that the increase in failure probability with the numerical increase in tubes is high enough to preclude reasonable reliable operation. This conclusion is based on

elementary probability estimates with failure probability nearly proportional to the number of tubes; and on the observed failure rate. Two immediate failures occurred with the eighteen tube module; several failures occurred in spans of zero to several operating hours for the six tube module; and three or four failures occurred during long duration runs in the order of days with the single tube.

7.0 PRETREATED URINE TEST RESULTS

It was desired to determine the performance of the dual layer membrane on pretreated urine. About 20 gallons of electrolytically pretreated urine were added to the system reservoir and processing initiated. The pH of the fluid was raised to ~6.0 by the addition of NaOH. A slight precipitate was noted. A membrane never exposed to waste was retrieved from storage. Its performance was nominally 82 percent at 0.2 cm/min flux.

Table IV shows the results obtained with urine processing. The sample U1F represents the raw feed, U2P is the initial product sample. As the run proceeded with product being collected, a seal leak developed. The outflow of leak and product together resulted in shutdown after having processed only 30 percent of the feed. So 64 liters were added, 19 liters of product were collected, 10 liters of concentrate remained in the system after shut down, and thus 35 liters escaped by the leak. Sample U4P represents the mixture of the last 8.2 liters of product, while U4c was drawn from the system residue.

During the initial part of the test when the rig was attended, the flux underwent the following variations:

Time hr:min	Temp. °C	Flux cc/min	Flux cm/min corrected to 349K
0	328	.153	.228
0:05	335	.174	.209
0:15	342	.175	.184
9:00	347	.100	.0965
13:20	349	.117	.117

The addition of feed here resulted again in reduction of flux by 2/3, followed apparently by a tendency to recover.

The rejection of important quantities are as follows:

	<u>Early in Test</u>	<u>Late in Test</u>
NH ₃	53%	57%
Urea	68%	68%
Conductivity	62%	54%

These data indicate the general tendency of the membrane to exhibit lower rejection at high concentration for solutes which are ion excluded. It is of some interest that for urea and NH₃ the rejections are still reasonably intact at values of concentration an order of magnitude larger than that of the residual concentrate produced from washwater.

Table IV. Urine Test Results

Determination	U1F	U2P	U4C	U4P
Chromium as Cr^{+6} , ppm				50
Silver as Ag, ppm				
Zinc as Zn, ppm				
Fluoride as F, ppm				.42
Nitrate as NO_3 , ppm	1450		1575	625
Sulfate as SO_4^{-2} , ppm				
Chloride as Cl^- , ppm				355
Conductivity (umho/cm)	18,500	7,100	19,000	8,700
TOC, ppm				
COD, ppm				
NH_3 , ppm	800	379	1050	450
Urea, ppm	2250	715	2850	920
pH	6.56	7.14	6.5	6.88
Inorganic Carbon, ppm				

8.0 REFERENCES

1. C.A. Brandon and J.C. Hester, "Feasibility Demonstration of High Temperature Hyperfiltration of Shower Water" NASA CR - 112127, Clemson University, 1972.
2. J.S. Johnson et al, "Hyperfiltration", Principles of Desalination, K.S. Spiegler et al editor, Academic Press, N.Y. 1966.
3. D.F. Putnam and G.W. Wells, "Definition of Reverse Osmosis Requirements for Spacecraft Washwater Recycling", McDonnell Douglas Astronautics Report MDC G 3780, November 1972.

APPENDIX A - Derivation of Mass Balance Relations

It is possible to use a hyperfiltration membrane in any several flow arrangements. Each of these flow arrangements results in a different quality product water. Two single stage steady flow arrangements and a batch processing arrangement are presented together with predictions of their performance. In each of these the recovery R is the ratio of product produced to feed supplied, and the system rejection is $(1 - \bar{C}_p/C_f)$. The value of mixed product concentration (\bar{C}_p) is a product water specification, while feed concentration (C_f) is characteristic of shower water. The membrane rejection $(1 - C_p/C_c)$ is the performance at a point measured by the local product concentration C_p and the local concentrate concentration.

The first arrangement, indicated in Figure 1a, is one in which the pressurized feed flow is contacted with a long narrow membrane channel in which the solute concentration increases as product is withdrawn. The differential equation which governs this situation is:

$$C_c (1 - \gamma) d\dot{m}_c + \dot{m}_c dC_c = 0 \quad (1)$$

C_c = concentrate concentration

γ = rejection

\dot{m}_c = mass flow of concentrate

Under assumption of constant rejection γ , integration yields

$$\frac{C_c}{C_f} = \left(\frac{1}{1 - R} \right)^{\gamma} = \left(\frac{\dot{m}_f}{\dot{m}_c} \right)^{\gamma} \quad (2)$$

A mass balance of solute in the feed, concentrate, and mixed product streams may be written as

$$\dot{m}_f C_f = \dot{m}_p \bar{C}_p + \dot{m}_c C_c = \dot{m}_f (R \bar{C}_p + (1 - R) C_c) \quad (3)$$

This equation may be solved for \bar{C}_p , the mixed product concentration as

$$1 - \gamma_s = \frac{\bar{C}_p}{C_f} = \frac{1}{R} \left[1 - (1 - R) \right]^{1 - \gamma} \quad (4)$$

Equation (4) is plotted in Figure A1, which indicates the recovery R which results in a certain level of system rejection with an assumed membrane rejection (γ).

A second arrangement is depicted in Figure 1b, wherein feed is introduced into a recirculating loop from which product and concentrate flow. The flow rate of rejected concentrate is adjusted to yield the desired recovery. The system is analysed here under the assumption that the product flow is much less than the loop flow. Under this assumption all positions in the membrane are exposed to equal concentration of solute. A simple equation for the mass

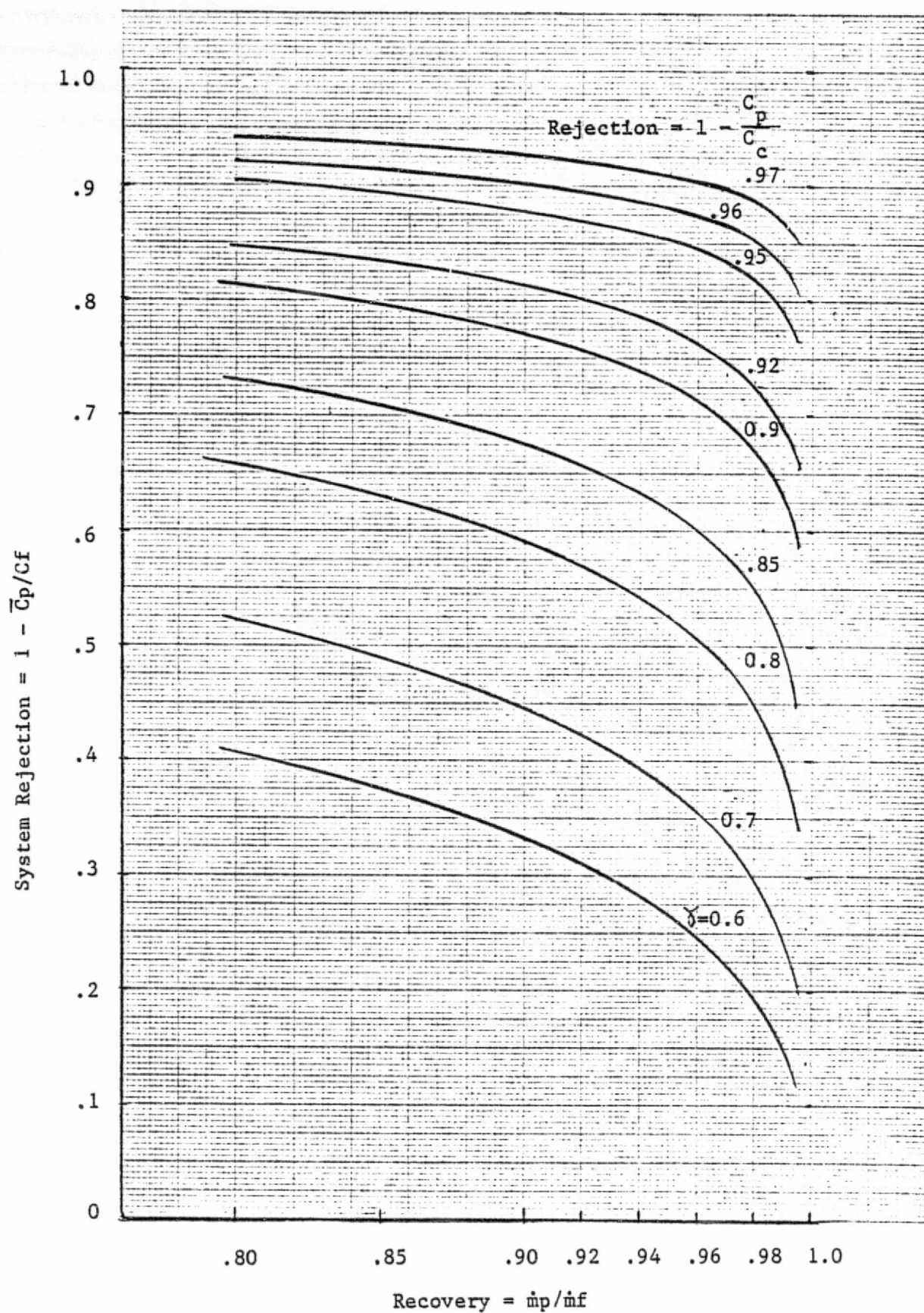


Figure A1 System Rejection vs Recovery for a Once-through Arrangement

balance of solute at steady state is:

$$\dot{m}_f C_f = \dot{m}_p C_p + \dot{m}_r C_c = \dot{m}_f (R C_p + (1 - R) C_c) \quad (5)$$

All product issues at the same quality; hence $C_p = \bar{C}_p$. The product quality is related to feed quality through:

$$1 - \gamma_s = \frac{\bar{C}_p}{C_f} = \frac{1 - \gamma R}{1 - R} \quad (6)$$

Equation (6) is plotted in Figure A2 with coordinates identical to those used for the once-through design. It is noted that lesser recoveries are uniformly possible for this arrangement than for the once-through arrangement.

A third arrangement is that a batch process wherein feed is gradually processed to a recovered product and concentrate. The concentrate passing through the membrane is mixed with the feed batch as shown in Figure 1c. The fluid is assumed to pass the membrane essentially without concentration. In time (dt) an amount of product (dm_p) is produced having solute mass $(1 - \gamma)C_c dm_p$. This flow is accompanied by a equal depletion of solute in the loop which may be expressed as $d(m_c C_c)$. Equating these gives

$$C_c dm_c + m_c dC_c = - (1 - \gamma) C_c dm_p.$$

Certainly $dm_c = dm_p$, which, substituted into the above and rearranging gives

$$m_c dC_c = \gamma C_c dm_c \quad (7)$$

Integration yields, signifying initial quantities by subscript f,

$$\frac{C_c}{C_f} = \left(\frac{m_f}{m} \right)^\gamma \quad (8)$$

But, the product aggregate m_p plus m must be m_f and m_p/m_f is the recovered fraction, R , so

$$\frac{C_c}{C_f} = \left(\frac{1}{1 - R} \right)^\gamma \quad (9)$$

Equation (9) is identical to equation (2) indicating a formal equivalence of the once-through arrangement and the batch process.

The highest recovery simple systems are either the once-through or the batch process. Higher recovery may be achieved in many different two-stage processes, at the expense of complexity and higher power requirements.

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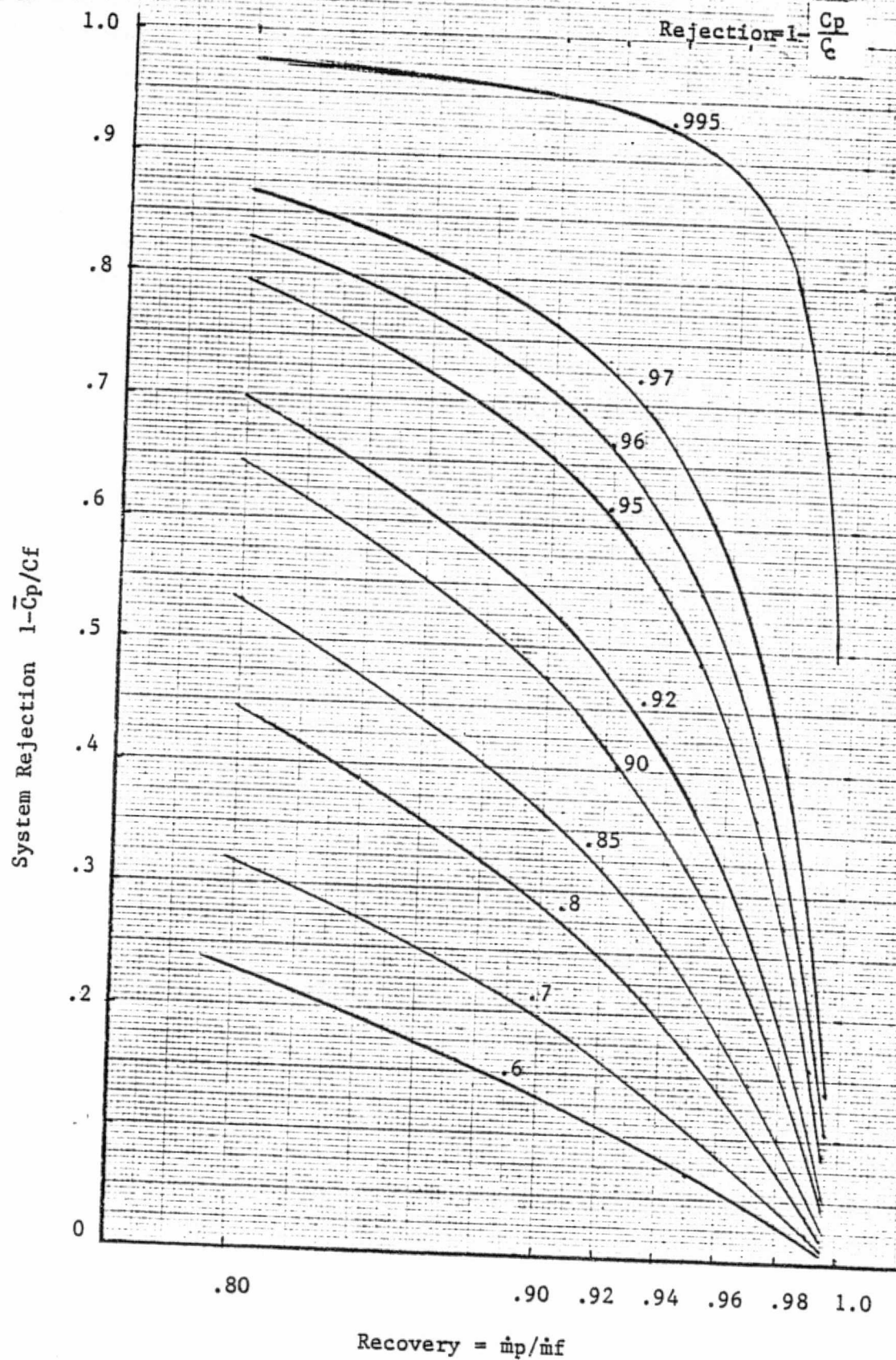


Figure A2 Rejection vs Recovery for a Recirculating Arrangement

APPENDIX B - Test Log Summary

The performance of individual membranes is denoted (X, Y)
X = percent rejection Y = flux in GFD. Flow of product in cc/min
may be multiplied by 2.4 to yield GFD.

<u>DATE</u>	<u>REMARKS</u>
4-20	Pump turned on.
4-22	Loop A-B wash.
4-23	Membrane 1 attempt - bad procedure and iron in system - membrane no good.
4-29	Membrane 2 attempt - poor procedure - good membrane, 94, 42.
5-6	Membrane 2 regenerated and stored 96, 35.
5-7	Membrane 3 formed 89, 69. Regen. of M3 - no improvement.
5-10	6 - 7 hole tube membrane 25%. M4 inspected for leakage.
5-15	Attempt M4 regen. 30% rejection.
5-15	Dismantle; broken tube found.
5-16	Order short center rod.
5-21	Reassemble 6-tube for M5.
5-22	Formation of M5 unsuccessful.
5-23	Order modifications to 6-tube unit.
5-24	ORNL M6 trial unsuccessful.
5-27	A - B wash.
5-28	Single tube M7 94, 39; 89, 64 overnight.
5-29	Regen. M7 to 94, 32 and store M7.
5-30	Six tube module installed for M8. Two successive fractures.
5-31	Two 19-tube outside-in bundles, M9. 88, 130.
6-4	M7 reinstalled and regenerated to 96, 27.

6-5 M7 degrade to 94, 28.

6-5 Add 21 gallons washwater.

6-6 to 6-7 First parametric run.

Parametric run consisted of T = 349°K; V = 8 M/sec; P = 65, 58, 51, 70 atmos.
Followed by T = 358°K, 368°K, Recheck 350°K; V = 8 M/sec; P = 65 atmos.
Followed by T = 350°K, V = 4, 2.8, 1.6 M/sec; P = 65 atmos.

6-8 System refilled with tap water. Discovered soap error.

6-10 Salt added to water. 78%, 55.

6-11 Tried wash (NaCO₃) and regeneration. 88, 31.

6-12 System washed. Installed 18 tube module.

6-13 Attempted formation. Fractured tubes on two successive trials at 20 atmos.

6-14 Installed 6 tube (7 holes each) module.

6-15 Attempt M8. Tube fracture. Reinstall single 7 hole tube.
Attempt M9. 71, 103.

6-17 Stored membrane M2 from 5-6-74 installed. Performance before was 95.6, 38. After 3 hours, performance is R = 95.4 @ 50 cc/min. Shower water added. Broke support within 1 hour.

6-18 Resolved to produce three acceptable membranes before further testing.

6-19 After washing loop attempt M10. 80.5, 129.

6-20 Regenerate M10. 89, 91. store M10.

6-21 Install new water filter: a Gulf replacing the DuPont. Attempt to clean system again. Start M11. R = 92 at 30 cc/min.

6-22 M12 is R = 87 @ 38 cc/min; store M11.

6-22 Start M12. R = 90 @ 12 cc/min.

6-24 Store M12 @ R = 88, 12 cc/min. Start M13. R = 87 @ 23 cc/min. Store M13.

6-25 Start M14. R = 80 @ 51 cc/min. Regenerate M14. R = 81 @ 44 cc/min. M14 not stored. Start M15. Procedure error.

6-25 Start M16. Before PAA addition, lost pressure and shut down.

6-26 Failure discovered to be an "O" ring. Start PAA layer, R = 83 @ 27 cc/min. Regenerate M16, R = 86 @ 19 cc/min. M16 stored.

6-27 Attempt to regenerate M13. M13 stored @ R = 88, 17.5 cc/min.

6-27 & 28 Wash system with Biz, followed by base/acid procedure.

6-28 Start M17, R = 86 @ 54 cc/min.

6-29 M17 is 80 @ 70 cc/min. Black powder noted in water.

6-29 M17 regenerated to R = 91 @ 27 cc/min. Store M17.

7-1 M11 reinstalled. R = 87 @ 42 cc/min.

7-1 Regenerate M11 to R = 96 @ 19 cc/min.

7-1 Add shower water to system and use M11.

7-2 & 3 Perform pressure, temp, and velocity variations.

7-3 Start concentration run.

7-4 Seal has failed on pump.

7-8 Receive seal and install. Start concentration run again.

7-11 Perform pressure survey.

7-12 Perform velocity survey.

7-13 End concentration run.

7-16 After salt water exposure, M11 performance is R = 80% @ 20 cc/min.

7-17 Reinstalled M17. Performance is R = 87 @ 31 cc/min.

7-18 Urine sample pH adjusted to ~6 and added to system.

7-19 After 30 percent recovery of product terminate test due to pump seal leakage.

APPENDIX C - NASA Analytical Methods

The following were employed as analytical equipment utilized by NASA-JSC.

Analysis	Method
pH Fluoride	Orion Model 801 Digital pH meter/Ionalyzer
Resistivity	Barnstead Model PM 50 Water Purity Indicator
Total Solids	Mettler Model B6 Analytical Balance
Organic Carbon	Beckman Model 915 Total Organic Carbon
Inorganic Carbon	Analyzer
Cadmium	Jarrell-Ash Atomic Absorption Spectrophotometer
Copper	Model 82500 series/Varian Carbon Rod Atomizer
Iron	Model 63
Lead	
Magnesium	
Manganese	
Mercury	
Nickel	
Potassium	
Silver	
Sodium	
Zinc	
Chromium	Colorimetric - Beckman ACTA CIII
Ammonia	UV-Visible Spectrophotometer
Nitrate	
Sulfate	
Chloride	